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SOME NOVEL TRIFLUOROMETHYL PHOSPHORUS CHEMISTRY

by



RONALD DAVID LEARY

A THESIS

SUBMITTED TO THE FACULTY OF GRADUATE STUDIES

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The undersigned certify that they have read, and
recommend to the Faculty of Graduate Studies for
acceptance, a thesis entitled

"SOME NOVEL TRIFLUOROMETHYL PHOSPHORUS CHEMISTRY"

submitted by RONALD DAVID LEARY in partial fulfil-
ment of the requirements for the degree of Master
of Science.

A C K N O W L E D G E M E N T S

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A B S T R A C T

Tris(trifluoromethyl)phosphine oxide reacts with hexamethyldisiloxane to form tris(trifluoromethyl)bis(trimethylsiloxy)phosphorane in good yield. This phosphorane is a relatively involatile colorless liquid stable at room temperature but decomposes at higher temperature. Several reactions of the new phosphorane were studied. The ^{19}F and ^1H n.m.r. spectra indicated that the most probable structure for the phosphorane at low temperature is probably the trigonal bipyramidal structure in which two trimethylsiloxy groups occupy the equatorial positions. A process such as pseudorotation provides a means of averaging the CF_3 and $\text{OSi}(\text{CH}_3)_3$ environments within themselves at ordinary temperature.

The compound bis(trifluoromethyl)trimethylsiloxyphosphine oxide produced on thermal decomposition of the above phosphorane, was also prepared from the reaction of chlorobis(trifluoromethyl)phosphine oxide with hexamethyldisiloxane in good yield. However acceptable yields of the less stable sulphur analogue bis(trifluoromethyl)-trimethylsilylthiophosphine sulphide could only be obtained from the rapid reaction of bis(trifluoromethyl)-dithiophosphoric acid with bis(trimethylsilyl)amine. Reactions of these pentavalent tetracoordinated phosphorus compounds were investigated.

The reaction of fluorobis(trifluoromethyl)phosphine with hexamethyldisiloxane at high temperature gave bis(trifluoromethyl)trimethylsiloxylphosphine almost quantitatively. Similarly the less stable sulphur analogue bis(trifluoromethyl)trimethylsilylthiophosphine was prepared in good yield from the reaction of chlorobis(trifluoromethyl)phosphine with hexamethyldisilthian. Several reactions of these tervalent tricoordinated phosphorus compounds were studied. Of particular interest was the reaction of dimethylamine with bis(trifluoromethyl)trimethylsiloxylphosphine which gave fluoroform and the novel compound dimethylaminotrifluoromethyltrimethylsiloxylphosphine.

The above compounds were characterized by chemical reactions, mass spectroscopy, including accurate mass measurements of some of the parent ions and infrared and nuclear magnetic resonance spectroscopy.

Reactions of tris(trifluoromethyl)phosphine with several alcohols, acids and amines were investigated. Only the amines reacted to any appreciable extent with tris(trifluoromethyl)phosphine giving fluoroform and the amino-phosphine compounds. Some new nuclear magnetic resonance data on the amino-phosphine was obtained.

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CHAPTER II N T R O D U C T I O N

Although the first compound containing a P-O-Si bridge was synthesized by the reaction of amorphous silicic acid with phosphorous acid ^{1,3} in 1883, it was not until 1944 that a simple organosilicon compound which contained the P-O-Si bridge, $[(CH_3)_3SiO]_3 P = O$ ^{2,3}, was reported. Then in subsequent years a number of papers were published concerning the preparation and properties of a number of compounds containing the P-O-Si and P-S-Si bridges. A comprehensive survey of these systems is the subject of a review by Chernyshev and Bugerenko.³

As summarized in the review ³, compounds containing one, two or three P-O-Si bridge systems are now well known, and many examples of both tervalent phosphino oxy-silanes [such as R_3SiOPR_2 , $(R_3SiO)_2PR$ and $(R_3SiO)_3P$] and pentavalent phosphoryl oxy-silanes [for example $(R_3SiO)_3 P = O$, $(R_3SiO)_2 P(O)R$ and $R_3SiOP(O)R_2$] (R = organic groups) have been prepared. In contrast, the P-S-Si bridge system has received little attention. The only reported compounds are of the type $R_3SiSP(S)R_2$ which are derivatives of the pentavalent thiophosphoryl system. No phosphines with P-S-Si bridges are known. Several pentavalent oxy-thio phosphorus compounds are known, all of which apparently prefer to exist in the P-O-Si bridge form rather than in

the isomeric P-S-Si bridge form (eg. $R_3SiOP(S)R_2$).

The synthesis⁴ of the new phosphorane $(CF_3)_3P[OSi(CH_3)_3]_2$ and the study of its reactions resulted in the need to establish the characteristics of trifluoromethyl phosphorus oxy-silanes and a systematic study of these systems and the fluorophosphoryl analogues has been undertaken. The absence of any known tervalent phosphorus compounds containing the P-S-Si bridge suggested that the study should be extended to include the phosphines and the first trivalent phosphorus thiosilane has been prepared and characterized.

CHAPTER II

MATERIALS, APPARATUS AND TECHNIQUES

The general features of the apparatus, materials and experimental techniques used in preparation and characterization of the compounds in this thesis will be described in this Chapter. Other special techniques required for particular experiments are described where appropriate.

1. Techniques

Infrared spectra were recorded on a Perkin-Elmer 337 (4000 cm^{-1} to 400 cm^{-1}) for rapid identification of compounds during separation procedures. Perkin-Elmer 421 (4000 cm^{-1} to 550 cm^{-1}) and Beckmann I.R.11 (600 cm^{-1} to 400 cm^{-1}) were used to provide infrared spectra of new compounds. Gas phase spectra were obtained in a 9 cm path-length cell equipped with potassium bromide windows affixed with Apiezon N grease. The purity of the new compounds used for the reported spectra was checked by n.m.r. spectra.

Mass spectra were recorded on A.E.I. MS-2 or MS-9 instruments operating at ionizing voltage of 70 e.v. The MS-9 was used for high resolution scans and accurate mass measurements. A room temperature inlet in the mass spectrometer was used to introduce all gaseous samples except in some cases where extreme reactivity made it desirable to use a specially designed ⁵ inlet system which permitted

the introduction of gaseous samples directly into the ionizing source chamber through the direct probe insertion lock. For low volatile compounds, the normal heated inlet system was used and for non-volatile compounds, the normal direct probe provided with the A.E.I. MS-9 system was used.

All n.m.r. spectra were recorded on Varian A56/60 or Varian HA-100 instruments. The proton spectra were obtained at 60 or 100 MHz, fluorine spectra at 56.4 or 94.1 MHz. All phosphorus spectra were obtained at 40.5 MHz on the 100 MHz instrument. Samples for n.m.r. measurements were prepared under vacuum by distilling an appropriate quantity of the compound and sufficient solvent into 5 mm o.d. medium wall sample tubes containing a capillary which held the reference compound. Proton and fluorine spectra were routinely recorded on samples containing an approximate 10% solution of the compound in CCl_3F or CCl_2F_2 . Good phosphorus spectra required solutions of 25% to 60% concentration. The chemical shifts of fluorine and hydrogen were measured relative to CCl_3F or tetramethylsilane (TMS) usually provided in a single capillary containing a 5% solution of TMS in CCl_3F . Phosphorus spectra were measured relative to a capillary of neat P_4O_6 .⁶ Each instrument was equipped with a Varian V6040 variable temperature controller which appeared to be accurate to within $\pm 5^\circ$ of the temperature indicated on the controller. The spin-tickling experiment was done on the HA-100 instrument operating at

94.1 MHz using a Hewlett-Packard model 200 AB audio oscillator to provide irradiation of the desired signals.

2. Vacuum Apparatus and Techniques

Standard vacuum techniques were used throughout. The system was constructed of Pyrex glass and vacuum cup stopcocks were lubricated with Apiezon N grease. A Leroy still⁷ was built into the system to aid in difficult separations. Gas phase molecular weights (M) were used to characterize volatile products, especially CF₃H.

Reactions were generally carried out in sealed Pyrex glass tubes of appropriate volumes of 15 cc, 50 cc, or 75 cc the choice depending on the maximum pressure expected from the reactions. High temperature reactions were done in large volumes in order to keep the pressure low.

The vapor pressures of the compounds were measured in a special all-glass grease-free microtensimeter⁸ with both ascending and descending temperatures as shown in Figure 1 below. The temperature was measured with an accurately calibrated mercury-filled thermometer. Pressures were read using a cathetometer graduated to 0.001 mm.

This microtensimeter was calibrated with water. The vapor pressure data, given in the Appendix, Table XV, is best described by the equation:

$$\log_{10} P_{\text{mm}} = 8.9135 - \frac{2244}{T}$$

which gives an extrapolated boiling point of 98.8°, a heat

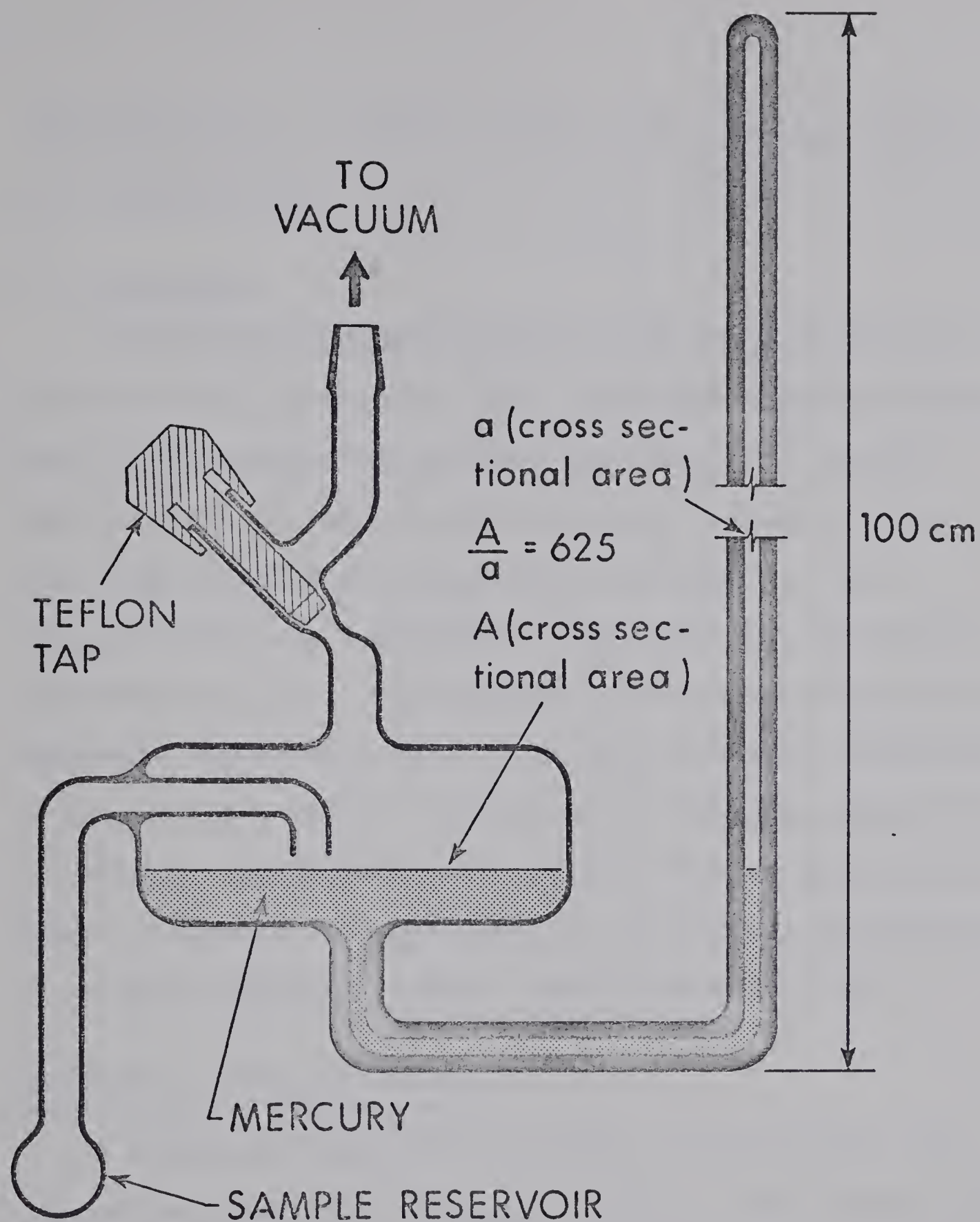


FIGURE 1. Grease-free Microtensimeter

of vaporization of 10268 cal/mole and a Trouton constant of 27.6 cal/mole deg.

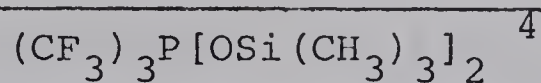
3. Materials

Trifluoromethyliodophosphines and $(\text{CF}_3)_3\text{P}$ were prepared from the reaction of CF_3I (Columbia Organic Chemicals) with red phosphorus at 220° for 48 hours.^{9,10} Vacuum fractionation of the volatile products through a series of cold traps gave CF_3PI_2 which was collected at -45° , $(\text{CF}_3)_2\text{PI}$ which was collected at -84° and $(\text{CF}_3)_3\text{P}$ which was collected at -116° . The remaining trifluoromethylphosphorus compounds required in this study were prepared according to literature methods. Commercially available chemicals of "Reagent" grade were used without further purification. Gaseous reagents were subjected to fractional condensation in vacuum in order to remove impurities before use.

Synthesis of $(\text{CH}_3)_3\text{SiN}(\text{CH}_3)_2$

A sample of $(\text{CH}_3)_3\text{SiCl}$ (0.145 g, 1.34 mmoles) was allowed to react with $(\text{CH}_3)_2\text{NH}$ (0.134 g, 2.97 mmoles) for one half hour. Vacuum fractionation of the volatile products gave $(\text{CH}_3)_3\text{SiN}(\text{CH}_3)_2$ (0.120 g, 1.11 mmoles) which was collected at both -63° and -84° and a material which passed the -84° trap that was not analysed.

CHAPTER III

Tris(trifluoromethyl)bis(trimethylsiloxy)phosphorane

Pentacoordinate halogenophosphorus compounds have been known for many years.¹¹ Only a few compounds are known however in which five organo or organometallic substituents are attached to phosphorus even if the pentacoordinate oxyphosphoranes^{12,13,14,15} are included in this classification. No trifluoromethyl phosphorus compounds with five non-halogen substituents have been reported. We report herein the synthesis and characterization of a pentacoordinate CF_3 phosphorus compound containing only CF_3 and $\text{OSi}(\text{CH}_3)_3$ substituents.

1. Preparation and Characterization of Tris(trifluoromethyl)bis(trimethylsiloxy)phosphorane

(a) From $(\text{CF}_3)_3\text{P}=\text{O}$ and $[(\text{CH}_3)_3\text{Si}]_2\text{O}$.

Tris(trifluoromethyl)phosphine oxide, $(\text{CF}_3)_3\text{P}=\text{O}$ ^{16,17} (0.525 g, 2.06 mmoles), containing a trace of $(\text{CF}_3)_3\text{P}$, and hexamethyldisiloxane $[(\text{CH}_3)_3\text{Si}]_2\text{O}$ (0.292 g, 1.81 mmoles) were allowed to react for twenty-two days at room temperature. The volatile products were transferred to a micro-reflux column¹⁸ in which the crude product was refluxed with the jacket maintained at -10° to -15° and the more volatile constituents removed in vacuum. The

least volatile fraction obtained initially was slightly impure $(\text{CF}_3)_3\text{P}[\text{OSi}(\text{CH}_3)_3]_2$ (0.719 g, 1.73 mmoles) containing a small quantity of $[(\text{CH}_3)_3\text{Si}]_2\text{O}$ (0.013 g, 0.08 mmoles). The latter was detected in the n.m.r. spectrum and the quantity involved was calculated from the observed peak heights. The more volatile fraction contained a mixture (0.084 g) of $(\text{CF}_3)_3\text{P} = \text{O}$, $(\text{CF}_3)_3\text{P}$ and $[(\text{CH}_3)_3\text{Si}]_2\text{O}$ as indicated by the i.r. spectrum. The desired phosphorane was obtained in ~99% purity (by n.m.r.) by repeated reflux distillations as described above and characterized by the reactions described below.

(b) Characterization of $(\text{CF}_3)_3\text{P}[\text{OSi}(\text{CH}_3)_3]_2$

The compound is a clear, colorless, relatively involatile liquid which is reasonably stable at room temperature. At higher temperature, the compound decomposed to give $(\text{CF}_3)_2\text{P}(\text{O})\text{OSi}(\text{CH}_3)_3$ and a variety of other products as discussed below.

The compound was characterized by its spectroscopic properties (i.r. Table II, and n.m.r. Table XIV, Appendix) by mass spectroscopy (Table I) and by the chemical reactions described below. The mass spectrum of $(\text{CF}_3)_3\text{P}[\text{OSi}(\text{CH}_3)_3]_2$ showed no parent ion, a result which is typical of pentacoordinated pentavalent phosphorus compounds.¹⁹ The strong ions at 351 and 347 which were identified by mass measurement(s) (calcd for $(\text{CF}_3)_2\text{FP}[\text{OSi}(\text{CH}_3)_3]\text{OSi}(\text{CH}_3)_2$ m/e

TABLE I

Mass Spectrum of $(\text{CF}_3)_3\text{P}[\text{OSi}(\text{CH}_3)_3]_2^a$

<u>m/e</u>	<u>I, %</u>	<u>Ion^d</u>	<u>m/e</u>	<u>I, %</u>	<u>Ion^d</u>
354	0.08	$\text{C}_7\text{H}_{15}\text{F}_7\text{PO}_2\text{Si}_2$	159	0.21	$\text{C}_2\text{H}_3\text{F}_3\text{POSi}$
353	0.63		157	0.03	$\text{C}_2\text{HF}_3\text{POSi}$
352	1.47		156	0.03	$\text{C}_3\text{H}_6\text{F}_2\text{POSi}$
351 ^c	8.0		155	0.39	
350	0.12	$\text{C}_8\text{H}_{18}\text{F}_6\text{PO}_2\text{Si}_2$	153	0.06	$\text{C}_3\text{H}_4\text{F}_2\text{POSi}$
349	0.32		152	0.06	$\text{C}_3\text{H}_2\text{F}_2\text{POSi}$
348	0.75		151	0.36	
347 ^c	3.83		150	0.14	
346	0.09	$\text{C}_8\text{H}_{17}\text{F}_6\text{PO}_2\text{Si}_2$	149	1.85	$\text{C}_5\text{H}_{15}\text{OSi}_2$
327	0.05	$\text{C}_8\text{H}_{17}\text{F}_5\text{PO}_2\text{Si}_2$	148	2.95	
311	0.03	$\text{C}_7\text{H}_{13}\text{F}_5\text{PO}_2\text{Si}_2$	147 ^c	18.5	
303	0.02	$\text{C}_5\text{H}_8\text{F}_6\text{PO}_2\text{Si}_2$	145	0.37	
302	0.03		144	0.70	$\text{C}_2\text{H}_6\text{F}_2\text{POSi}$
301	0.21		143	8.82	
297	0.09	$\text{C}_6\text{H}_{11}\text{F}_5\text{PO}_2\text{Si}_2$	141	0.13	$\text{C}_3\text{H}_9\text{FPOSi}$
261	0.02	$\text{C}_6\text{H}_{11}\text{F}_3\text{PO}_2\text{Si}_2$	140	0.31	
260	0.05		139	3.83	
259	0.55		137	0.10	$\text{C}_3\text{H}_7\text{FPOSi}$
213 ^c	0.17	$\text{C}_5\text{H}_{15}\text{FPO}_2\text{Si}_2$	135	0.18	$\text{C}_3\text{H}_5\text{FPOSi}$
210	0.03	$\text{C}_3\text{H}_6\text{F}_4\text{PO}_2\text{Si}$	133	0.40	$\text{C}_4\text{H}_{13}\text{OSi}_2$
209 ^c	0.21		132	0.11	$\text{C}_4\text{H}_{11}\text{OSi}_2$
166	0.10	$\text{C}_5\text{H}_{12}\text{FPOSi}$	131	0.82	

continued.....

TABLE I (continued)

129	0.09	$\text{CH}_4\text{F}_2\text{POSi}$	91	$\left\{ \begin{array}{l} 0.16 \\ 0.37 \end{array} \right\}$	PO_2Si
128	0.03	$\text{CH}_3\text{F}_2\text{POSi}$	89	0.09	$\text{C}_3\text{H}_9\text{SiO}$
127	0.12	$\text{CH}_2\text{F}_2\text{POSi}$	87	0.20	$\text{C}_3\text{H}_7\text{SiO}$
125	0.22	$\text{C}_2\text{H}_7\text{FPOSi}$	82	0.07	$\left. \begin{array}{l} \\ \\ \end{array} \right\} \text{H}_3\text{FPSi}$
124	0.07	$\text{C}_2\text{H}_6\text{FPOSi}$	81	0.60	
123	0.10	$\text{C}_2\text{H}_5\text{FPOSi}$	79	0.54	
121	0.70	$\text{C}_2\text{H}_3\text{FPOSi}$	78	1.0	$\left. \begin{array}{l} \\ \end{array} \right\} \text{H}_2\text{POSi}$
119	0.80	$\text{C}_3\text{H}_{11}\text{OSi}_2$	77	14.5	
117	0.23	$\text{C}_3\text{H}_9\text{OSi}_2$	76	$\left\{ \begin{array}{l} 0.39 \\ 0.16 \end{array} \right\}$	$\text{C}_2\text{H}_2\text{FP}$
116	0.07	$\text{H}_3\text{F}_2\text{POSi}$	75	1.32	
115	0.10	$\text{H}_2\text{F}_2\text{POSi}$	74	1.75	$\left. \begin{array}{l} \\ \end{array} \right\} \text{C}_3\text{H}_9\text{Si}$
113	$\left\{ \begin{array}{l} 0.05 \\ 0.07 \end{array} \right\}$	F_2POSi	73	$\left\{ \begin{array}{l} 21.5 \\ 0.2 \end{array} \right\}$	
107	0.07	CHFPOSi	72	$\left\{ \begin{array}{l} 1.45 \\ 0.1 \end{array} \right\}$	$\text{H}_3\text{F}_2\text{P}$
105	$\left\{ \begin{array}{l} 0.11 \\ 0.06 \end{array} \right\}$	$\text{C}_2\text{H}_9\text{Si}_2\text{O}$	71	0.20	$\text{H}_2\text{F}_2\text{P}$
103	0.23	$\text{C}_2\text{H}_7\text{Si}_2\text{O}$	70	0.16	HF_2P
102	0.10	$\left. \begin{array}{l} \\ \\ \end{array} \right\} \text{C}_2\text{H}_4\text{Si}_2\text{O}$			
101	0.10				
100	0.56				
97	0.18	H_3FPOSi			
95	0.20	HFPOSi			
94	0.04	$\left. \begin{array}{l} \\ \end{array} \right\} \text{H}_2\text{PO}_2\text{Si}$			
93	0.65				
92	0.27	HPO_2Si			

continued.....

FOOTNOTES TO TABLE I

- (a) Sample was introduced through heated inlet system to get desired spectrum.
 - (b) Intensities are expressed as percent total ionization, defined as $\sum (\text{Int})_n$ where n refers to all ions with $m/e > 69$ whose intensity is 0.1% of the base peak. Left hand brackets enclose reduced intensities of multiplet components at given m/e .
 - (c) The identity of these peaks was established by mass measurement under high resolution.
 - (d) Ions are listed only once in the Table under the most general designation.
-

TABLE IIInfrared Spectrum of $(\text{CF}_3)_3\text{P}[\text{OSi}(\text{CH}_3)_3]_2^a$

2967 ^b	m	$\nu(\text{C-H})$	1070	m	$\nu(\text{O-Si})$
2902 ^b	w	$\nu(\text{C-H})$	1011	w	
1264	m	$\delta(\text{Si-CH}_3)$	853	s	$\nu(\text{Si-C})$
1208	s	$\nu(\text{C-F})$	764	w	$\delta_s(\text{CF}_3)$
1185	vs	$\nu(\text{C-F})$	599	s	$\delta_{as}(\text{CF}_3)$
1168	m,sh	$\nu(\text{C-F})$	588	w	
1120	s	$\nu(\text{C-F})$			

s = strong, m = medium, w = weak, v = very, sh = shoulder
 ν = stretch, δ = deformation, as = antisymmetric,
s = symmetric

a

The i.r. cell plates were covered with a thin layer of paraffin wax and a liquid phase was present in the 9 cm i.r. cell.

b

These were obtained from another spectrum which did not have the paraffin layer on the i.r. plates.

351.0236; found m/e 351.0233: calcd for $(\text{CF}_3)_2\text{P}[\text{OSi}(\text{CH}_3)_3]_2$ m/e 347.0487; found m/e 347.0481) have a composition which strongly suggests that they arise from the fragmentation of the unobserved parent phosphorane $(\text{CF}_3)_3\text{P}[\text{OSi}(\text{CH}_3)_3]_2$ in the two pathways shown in Figure 2.

2. Reactions of Tris(trifluoromethyl)bis(trimethylsiloxy)-phosphorane.

(a) With Water

A sample of $(\text{CF}_3)_3\text{P}[\text{OSi}(\text{CH}_3)_3]_2$ (0.126 g, 0.30 mmoles) was allowed to react with 0.6 cc of distilled H_2O . Vacuum fractionation of the volatile products gave CF_3H (0.021 g, 0.30 mmoles) and a mixture (0.054 g) of $[(\text{CH}_3)_3\text{Si}]_2\text{O}$ and H_2O in the ratio 38:1 (by n.m.r.). Neutralization of the aqueous solution with sodium hydroxide gave a solution which contained the $(\text{CF}_3)_2\text{PO}_2^-$ anion as indicated by the n.m.r. spectrum.²⁰

(b) Alkaline Hydrolysis

$(\text{CF}_3)_3\text{P}[\text{OSi}(\text{CH}_3)_3]_2$ (0.106 g, 0.25 mmoles) and excess degassed 10% NaOH solution were allowed to react for 7 days at room temperature. Vacuum fractionation of the volatile products gave CF_3H (0.034 g, 0.49 mmoles) and an unseparated mixture of H_2O and $[(\text{CH}_3)_3\text{Si}]_2\text{O}$. The remaining sodium salt solution contained the CF_3PO_3^- ion according to the n.m.r. spectrum.²⁰

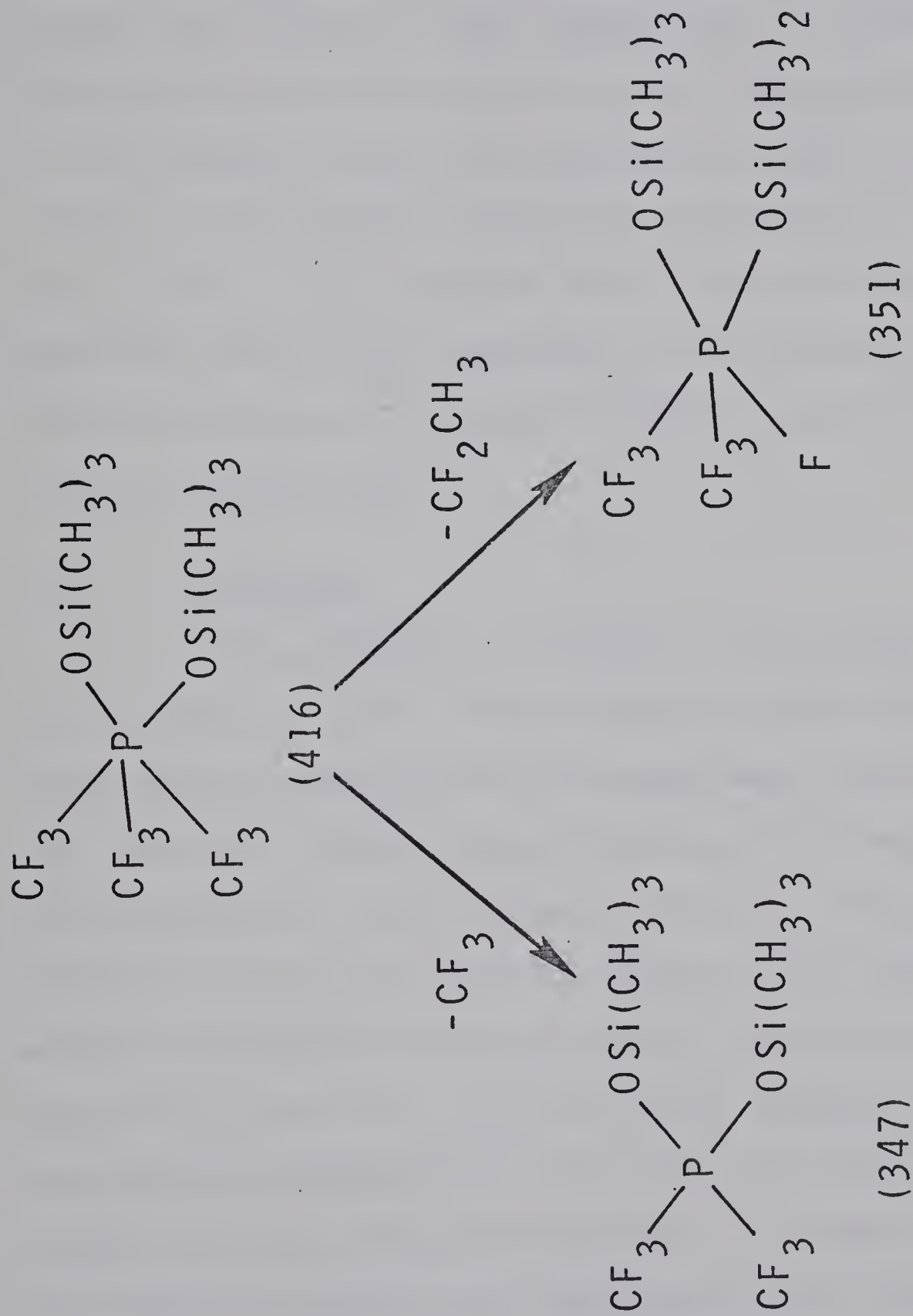


FIGURE 2. A possible fragmentation pattern of the unobserved parent phosphorane $(\text{CF}_3)_3\text{P}[\text{OSi}(\text{CH}_3)_3]_2$ which could explain its non-appearance. Formula of products have been determined by accurate mass measurement however structures are only proposals.

(c) With Dimethylamine

A sample of $(\text{CF}_3)_3\text{P}[\text{OSi}(\text{CH}_3)_3]_2$ (0.137 g, 0.33 mmoles) was allowed to react with $(\text{CH}_3)_2\text{NH}$ (0.060 g, 1.33 mmoles) for 7 days at room temperature. Vacuum fractionation of the volatile products gave $(\text{CH}_3)_3\text{SiN}(\text{CH}_3)_2$ (0.076 g, 0.65 mmoles) which was collected at -84° , $(\text{CH}_3)_2\text{NH}$ (0.014 g, 0.31 mmoles) which was collected at -116° , and CF_3H (0.024 g, 0.34 mmoles) which was collected at -196° . The white solid which remained in the reaction tube was identified as the $(\text{CF}_3)_2\text{P}(\text{O})\text{O}^-\text{H}_2\text{N}^+(\text{CH}_3)_2$ salt by n.m.r.²⁰ and mass spectroscopy.

(d) Pyrolysis

$(\text{CF}_3)_3\text{P}(\text{OSiMe}_3)_2$ (0.121 g, 0.29 mmoles) was heated for 4.5 days at 100° . Fractionation of the volatile products gave mixtures (0.053 g) which were collected at both -45° and -63° , $[(\text{CH}_3)_3\text{Si}]_2\text{O}$ (0.016 g, 0.10 mmoles) which was collected at -84° , a mixture (0.047 g) which was collected at -116° and a mixture (0.006 g) of COF_2 and other as yet unidentified compounds which was collected at -196° . Analysis of the -45° , -63° and -116° mixtures by n.m.r. spectroscopy indicated the presence of a variety of compounds with the chemical shifts (ϕ , τ), coupling constants (J) and their heights (h) indicated in the list below. Identities of the compounds are also indicated in the list where clear assignments can be made.

^1H			^{19}F				Identity
τ	h (cm)	ϕ	J (cps)	h^b (cm)	App ^a		
-45° and -63° trap	9.47	5.90	73.1	121	9.25	c	$(\text{CF}_3)_2\text{P}(\text{O})\text{OSi}(\text{CH}_3)_3$
	9.57	1.65	69.6	109	7.10	c	$(\text{CF}_3)_3\text{P}[\text{OSi}(\text{CH}_3)_3]_2$
	9.83	0.65	-	-	-	-	$[(\text{CH}_3)_3\text{Si}]_2\text{O}$
			66.0	113	0.40	c	$(\text{CF}_3)_3\text{P}=\text{O}$
-116° trap	9.72	5.4	-	-	-	-	?
	9.83	1.6	-	-	-	-	$[(\text{CH}_3)_3\text{Si}]_2\text{O}$
			66.1	113	5.65	c	$(\text{CF}_3)_3\text{P}=\text{O}$
			50.8	85	4.73	c	$(\text{CF}_3)_3\text{P}$
			67.7	-	2.30	d	?
			158	7	0.80	e	$(\text{CH}_3)_3\text{SiF}$

^a Appearance of spectrum due to spin-spin splitting pattern.

^b Total integrated intensity of spin splitting pattern.

^c Doublet

^d Singlet

^e Septet

(e) With Methyl Mercaptan

The compound $(\text{CF}_3)_3\text{P}[\text{OSi}(\text{CH}_3)_3]$ (0.070 g, 0.17 mmol) and CH_3SH (0.080 g, 1.66 mmol) were allowed to react at room temperature for 7 days. Vacuum fractionation of the volatile products gave a mixture (0.068 g) of $(\text{CF}_3)_3\text{P}[\text{OSi}(\text{CH}_3)_3]_2$, $(\text{CF}_3)_3\text{P}=\text{O}$, $[(\text{CH}_3)_3\text{Si}]_2\text{O}$ and an un-

identified CF_3P compound ($\phi = 69.0$, $J = 105$ Hz) in the ratio 39:1:2: 1.4 (by n.m.r.) which was collected at -63° and another mixture of CH_3SH , $(\text{CF}_3)_3\text{P}=\text{O}$ and a small amount of an unidentified compound (indicated by i.r.) which passed through the -63° trap to collect at -196° .

(f) With Chlorine

A sample of $(\text{CF}_3)_3\text{P}[\text{OSi}(\text{CH}_3)_3]_2$ (0.162 g, 0.39 mmoles) was allowed to react with Cl_2 (0.030 g, 0.42 mmoles) for six days at room temperature. Vacuum fractionation of the volatile products gave a mixture (0.137 g) of $(\text{CF}_3)_3\text{P}[\text{OSi}(\text{CH}_3)_3]_2$, $(\text{CF}_3)_3\text{P}=\text{O}$, $[(\text{CH}_3)_3\text{Si}]_2\text{O}$ and unidentified compounds ($\phi = 68.9$, $J = 106$ Hz; $\phi = 72.8$, $J = 123$ Hz; $\tau = 9.43$; 9.45 + others in ^1H spectra) in the ratio 8.4:1.1:~0.1:~1.1 (by n.m.r. taking all unidentified compounds together and assuming $(\text{CF}_3)_2\text{P}$ structure) which was collected at -45° , a mixture (0.007 g) of $(\text{CH}_3)_3\text{SiCl}$ and $(\text{CF}_3)_3\text{P}=\text{O}$ which was collected at -116° and a mixture (0.019 g) of HCl , Cl_2 , $(\text{CF}_3)_3\text{P}=\text{O}$ and CF_3H which was collected at -196° .

In another reaction $(\text{CF}_3)_3\text{P}[\text{OSi}(\text{CH}_3)_3]_2$ (0.105 g, 0.25 mmoles) and Cl_2 (0.110 g, 1.55 mmoles) were allowed to react in a -76° bath which was allowed to warm to room temperature slowly. After 7 days at room temperature, vacuum fractionation of the volatile products gave a mixture (0.043 g) of $(\text{CF}_3)_3\text{P}[\text{OSi}(\text{CH}_3)_3]_2$, $(\text{CF}_3)_3\text{P}=\text{O}$, $[(\text{CH}_3)_3\text{Si}]_2\text{O}$ and an unidentified CF_3P compound ($\phi = 69.0$, $J = 106$ Hz,

$\tau = 9.68$) 21:1:1:~4 (by n.m.r. assuming $(\text{CF}_3)_2\text{P}$ structure for the unknown compound) which was collected at -63° , a mixture (0.018 g) of $(\text{CF}_3)_3\text{P}=\text{O}$ and $(\text{CH}_3)_3\text{SiCl}$ which was collected at -116° and a mixture (0.093 g) of Cl_2 , HCl and trace of an unidentified compound (indicated by i.r.) which was collected at -196° . The colorless oily liquid of low volatility which remained in the reaction tube was dissolved in CD_3CN and the n.m.r. spectrum showed several ^1H resonances but no ^{19}F resonance signals.

(g) With Anhydrous HCl

A sample of $(\text{CF}_3)_3\text{P}[\text{OSi}(\text{CH}_3)_3]_2$ (0.324 g, 0.79 mmols) was allowed to react with HCl (0.117 g, 3.25 mmols) for 6 days at room temperature. Vacuum fractionation of the volatile products gave a mixture (0.234 g) of $(\text{CF}_3)_3\text{P}[\text{OSi}(\text{CH}_3)_3]_2$, $[(\text{CH}_3)_3\text{Si}]_2\text{O}$, with a variety of unidentified compounds which were collected at -63° , mixtures (0.108 g) of $(\text{CH}_3)_3\text{SiCl}$, $(\text{CF}_3)_3\text{P}=\text{O}$ and $[(\text{CH}_3)_3\text{Si}]_2\text{O}$ which were collected in the -84° , -116° and -132° traps. The most volatile fraction contained HCl (0.096 g, 2.74 mmols) (calcd. for HCl M, 36; found M, 39). A white solid and a colorless oil remained in the reaction tube.

(h) With Methanol

$(\text{CF}_3)_3\text{P}[\text{OSi}(\text{CH}_3)_3]_2$ (0.133 g, 0.32 mmols) was allowed to react with an excess of CH_3OH (0.025 g, 0.78 mmols) for 7 days at room temperature. Vacuum fractionation of

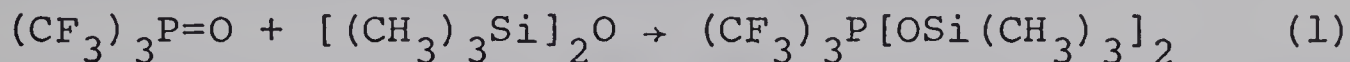
the volatile products gave mixture (0.125 g) which were first collected in both the -45° and -63° traps and another mixture (0.024 g) which passed through the -63° trap. Analysis of these mixtures by n.m.r. spectroscopy indicated the presence of a variety of compounds with the following chemical shifts (ϕ, τ), coupling constants (J), and peak heights (h). Identities of the compounds are indicated in the list below where clear assignments can be made.

¹ H		¹⁹ F					
(A) <u>Material Condensed at -63°</u>							
τ —	h (cm)	ϕ —	J (cps)	h^b (cm)	App ^a —	Identity —	
6.37	1.2					CH ₃ OH	
9.59	6.7	69.7	109	7.7	d	(CF ₃) ₃ P[OSi(CH ₃) ₃] ₂	
9.73	0.4					?	
9.87	0.6					[(CH ₃) ₃ Si] ₂ O	
		66.0	112	1.7	d	(CF ₃) ₃ P=O	
		66.5	102	1.2	d	?	
		69.3	103	2.2	d	?	
		73.7	114	2.9	d	?	
(B) <u>Material Volatile at -63°</u>							
6.38	1.1					CH ₃ OH	
6.58	2.9					?	
9.74 ^c	1.0	158	7.5	0.6	e	(CH ₃) ₃ SiF	
9.87	3.5					[(CH ₃) ₃ Si] ₂ O	
		78.7	80	1.4	d	CF ₃ H	
		83.0	74	1.0	d	?	

- a Appearance of spectrum due to spin-spin splitting pattern.
 - b Total integrated intensity of spin splitting pattern
 - c $J = 7.5$ cps septet
 - d doublet
 - e septet
-

3. Results and Discussion

The reaction of $(\text{CF}_3)_3\text{P}=\text{O}$ with $[(\text{CH}_3)_3\text{Si}]_2\text{O}$ at room temperature gave the novel compound $(\text{CF}_3)_3\text{P}[\text{OSi}(\text{CH}_3)_3]_2$ according to eqn (1).



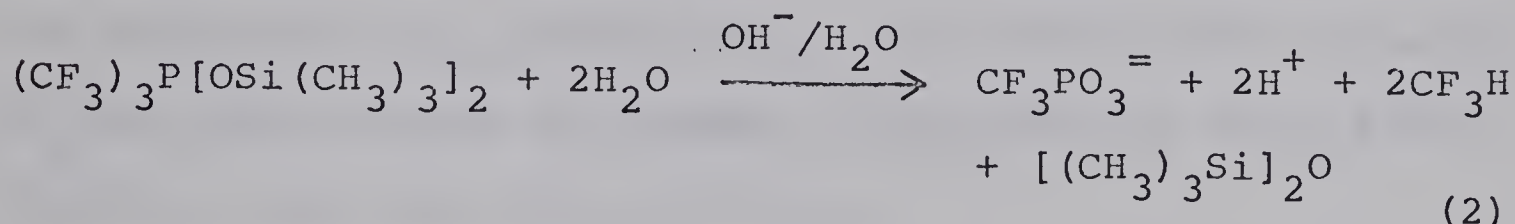
It is notable that the strong $\text{P}=\text{O}$ bond has been sacrificed with the formation of two $\text{P}-\text{O}-\text{Si}$ bridge bonds in this reaction. This result reflects the greater strength of two $\text{P}-\text{O}-\text{Si}$ bridges as compared to the combined strength of the $\text{P}=\text{O}$ and the $\text{Si}-\text{O}-\text{Si}$ bonds in the parent molecules. It is possible that strong π bonding contributes significantly to the strength and stability of the $\text{P}-\text{O}-\text{Si}$ bridge bonds.

It has been shown recently in this laboratory²¹ that the above reaction is not readily generalized since $(\text{CF}_3)_3\text{P}=\text{S}$ did not react at room temperature to give a penta-coordinated compound with $[(\text{CH}_3)_3\text{Si}]_2\text{S}$. Furthermore, reaction of $\text{F}_3\text{P}=\text{O}$ with $[(\text{CH}_3)_3\text{Si}]_2\text{O}$ gave only $\text{F}_2\text{P}(\text{O})\text{OSi}(\text{CH}_3)_3$ at room temperature and $\text{R}_3\text{P}=\text{S}$ ($\text{R} = \text{F}, \text{CF}_3$) compounds did not react with $[(\text{CH}_3)_3\text{Si}]_2\text{O}$ at room temperature.²¹ Phosphoryl fluoride and $[(\text{CH}_3)_3\text{Si}]_2\text{S}$ gave only a trace of $(\text{CH}_3)_3\text{SiF}$ at 110° .²¹

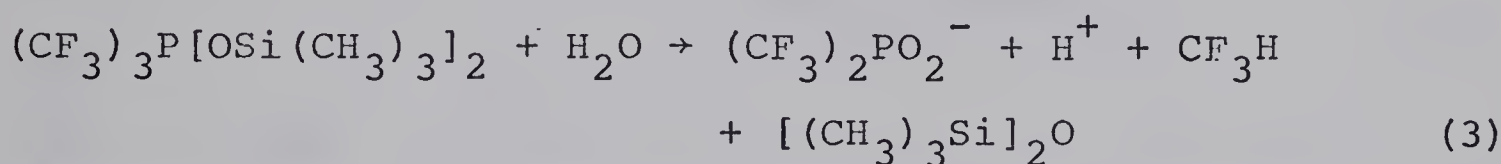
The chemical behavior of $(\text{CF}_3)_3\text{P}[\text{OSi}(\text{CH}_3)_3]_2$ agrees with the proposed formulation as a tris(trifluoromethyl)

phosphorus compound containing a pentavalent, pentacoordinated phosphorus atom. Alkaline hydrolysis of

$(\text{CF}_3)_3\text{P}[\text{OSi}(\text{CH}_3)_3]_2$ gave two molar equivalents of CF_3H , one molar equivalent of $[(\text{CH}_3)_3\text{Si}]_2\text{O}$ and one molar equivalent of the CF_3PO_3^- ion according to eqn (2).

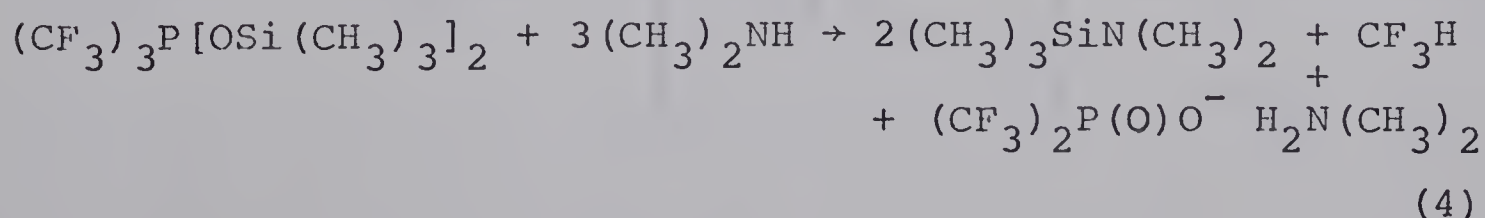


Furthermore the reaction of $(\text{CF}_3)_3\text{P}[\text{OSi}(\text{CH}_3)_3]_2$ with neutral water gave one molar equivalent each of CF_3H , $[(\text{CH}_3)_3\text{Si}]_2\text{O}$ and the $(\text{CF}_3)_2\text{PO}_2^-$ ion according to eqn (3).

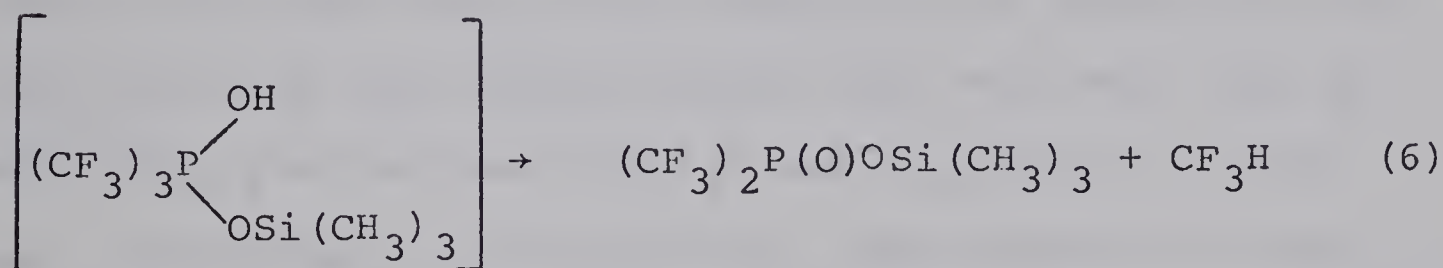
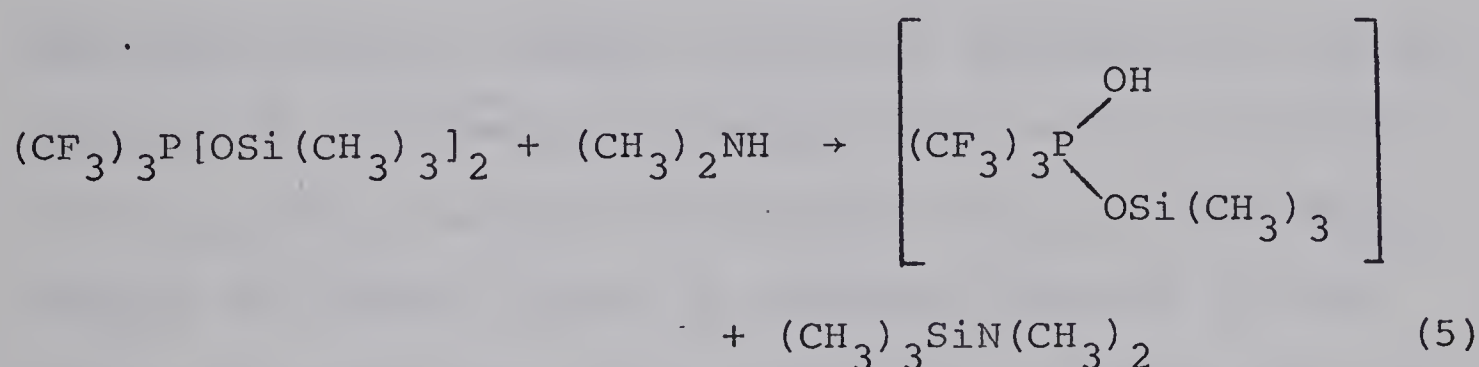


Both the neutral and alkaline hydrolysis results of $(\text{CF}_3)_3\text{P}[\text{OSi}(\text{CH}_3)_3]_2$ are characteristic of the behaviour of a pentavalent trifluoromethyl phosphorus compound.²⁰

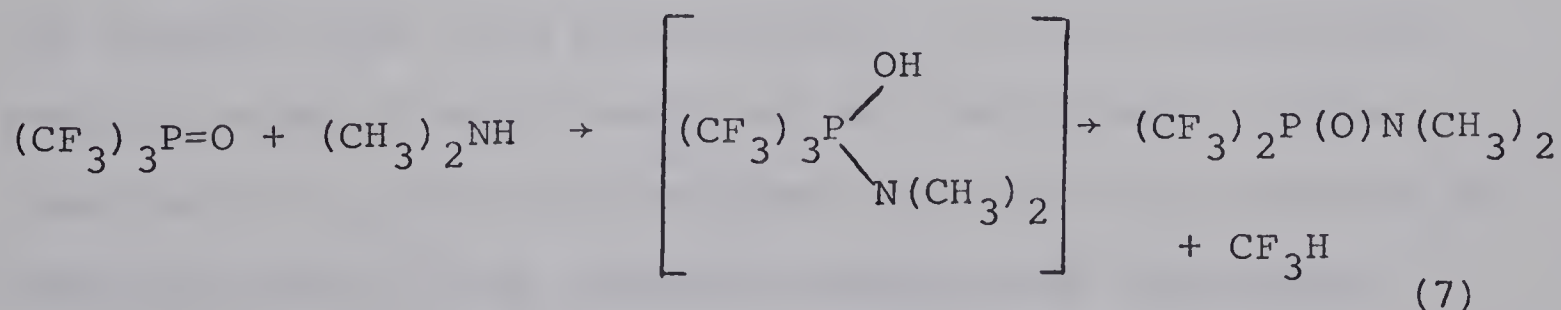
The reaction of dimethylamine with $(\text{CF}_3)_3\text{P}[\text{OSi}(\text{CH}_3)_3]_2$ gave two moles of $(\text{CH}_3)_3\text{SiN}(\text{CH}_3)_2$, one mole of CF_3H and a white salt formulated as the dimethylamine salt of $(\text{CF}_3)_2\text{PO}_2\text{H}$. The stoichiometry of the reaction is expressed in eqn (4).



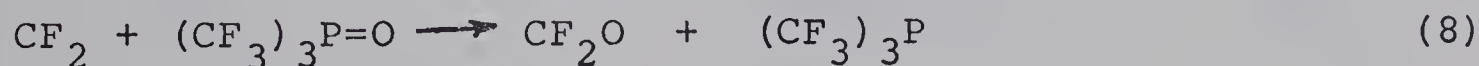
The reaction pathway probably involves the attack of $(\text{CH}_3)_2\text{NH}$ on the silicon atom in $(\text{CF}_3)_3\text{P}[\text{OSi}(\text{CH}_3)_3]_2$ followed by cleavage of the O-Si bond according to eqn (5). The unstable intermediate compound $(\text{CF}_3)_3\text{P}(\text{OH})\text{OSi}(\text{CH}_3)_3$ then rearranges to give $(\text{CF}_3)_2\text{P}(\text{O})\text{OSi}(\text{CH}_3)_3$ as in eqn (6). The resultant $(\text{CF}_3)_2\text{P}(\text{O})\text{OSi}(\text{CH}_3)_3$ then reacts with two moles of $(\text{CH}_3)_2\text{NH}$ as shown in Chapter IV to give the $(\text{CF}_3)_2\text{P}(\text{O})\text{O}^-$ $\text{H}_2\text{N}(\text{CH}_3)_2$ salt and $(\text{CH}_3)_3\text{SiN}(\text{CH}_3)_2$:



This probable pathway is favored since a similar intermediate $[(\text{CF}_3)_3\text{P}(\text{OH})\text{N}(\text{CH}_3)_2]$ can be proposed in the rapid reaction of $(\text{CH}_3)_2\text{NH}$ with $(\text{CF}_3)_3\text{P}=\text{O}$ which would then decompose to give the observed ²² products $(\text{CF}_3)_2\text{P}(\text{O})\text{N}(\text{CH}_3)_2$ and CF_3H according to eqn (7).



The compound $(\text{CF}_3)_3\text{P}[\text{OSi}(\text{CH}_3)_3]_2$ was found to decompose thermally at 100° yielding $(\text{CF}_3)_2\text{P}(\text{O})\text{OSi}(\text{CH}_3)_3$, $[(\text{CH}_3)_3\text{Si}]_2\text{O}$, CF_2O , $(\text{CH}_3)_3\text{SiF}$, $(\text{CF}_3)_3\text{P}$, $(\text{CF}_3)_3\text{P}=\text{O}$ plus other as yet unidentified compounds. The products $(\text{CF}_3)_3\text{P}=\text{O}$ and $[(\text{CH}_3)_3\text{Si}]_2\text{O}$ are of course the starting materials for the synthesis of the five coordinate compound and their generation could indicate that the formation reaction (eqn 1) is an equilibrium process. The remaining products however require a decomposition of the phosphorane by alternate pathways such as the evolution of $(\text{CH}_3)_3\text{SiCF}_3$ leaving the molecule $(\text{CF}_3)_2\text{P}(\text{O})\text{OSi}(\text{CH}_3)_3$. Perhaps the former, which is probably unstable at the relatively high temperature employed here decomposes to $(\text{CH}_3)_3\text{SiF}$ and CF_2 radicals which then may react (eqn 8) with $(\text{CF}_3)_3\text{P}=\text{O}$ to form $(\text{CF}_3)_3\text{P}$ and CF_2O both of which were identified in the products. The unidentified compounds could arise from reactions of the CF_2 radical with the various compounds that are present.

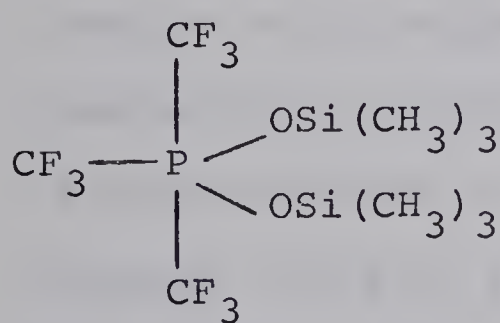


Methanol, methyl mercaptan, chlorine and anhydrous HCl reacted with $(\text{CF}_3)_3\text{P}[\text{OSi}(\text{CH}_3)_3]_2$ to give a variety of products some of which could not be identified. In the reaction of Cl_2 with the compound some HCl was recovered indicating that Cl_2 had probably reacted with the methyl groups in $(\text{CF}_3)_3\text{P}[\text{OSi}(\text{CH}_3)_3]_2$. This seems reasonable

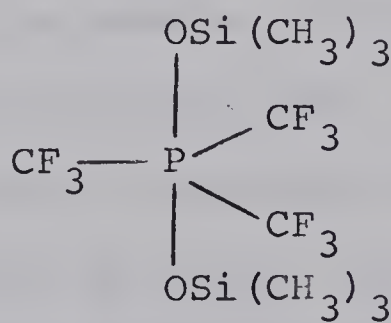
since Cl_2 was reported to react with $[(\text{CH}_3)_3\text{Si}]_2\text{O}$ to give HCl and $(\text{CH}_3)_3\text{SiOSi}(\text{CH}_3)_2\text{CH}_2\text{Cl}$.¹⁸ Complete investigations were not carried out.

4. Structure of the Phosphorane

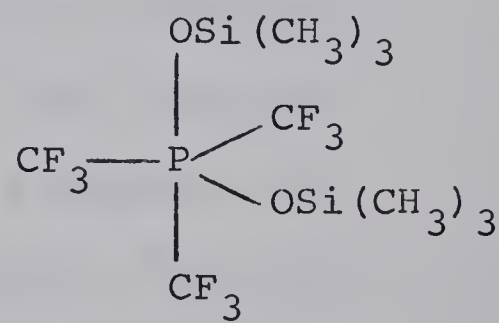
According to Muetterties and Schunn¹¹, the most likely geometry for a pentavalent, pentacoordinated phosphorus atom is a trigonal bipyramid model as in Figure 3. The possible arrangements of CF_3 and $\text{OSi}(\text{CH}_3)_3$ groups within the compound $(\text{CF}_3)_3\text{P}[\text{OSi}(\text{CH}_3)_3]_2$ are (1) a structure with two equatorial $\text{OSi}(\text{CH}_3)_3$ groups (I), (2) one with two axial $\text{OSi}(\text{CH}_3)_3$ groups (II) and (3) finally another one having one $\text{OSi}(\text{CH}_3)_3$ in the equatorial position and the other $\text{OSi}(\text{CH}_3)_3$ in the axial position (III) according to Figure 3.



(I)



(II)



(III)

FIGURE 3

The room temperature ^{31}P n.m.r. spectrum shows an eight

line pattern (Table XIV, Appendix) centred at +205 ppm vs P_4O_6 with an intensity distribution in good agreement with that expected for the central eight lines of a ten line pattern arising from nine equivalent fluorine atoms thus confirming the presence of three CF_3 groups on phosphorus.

At room temperature the 1H n.m.r. spectrum shows a moderately broad singlet (Table XIV, Appendix) due to equivalent $OSi(CH_3)_3$ groups which do not show observable coupling to phosphorus. On cooling the 1H n.m.r. spectrum to -115° , the singlet remained unchanged indicating that the $OSi(CH_3)_3$ groups are equivalent and that structure (III) probably does not occur.

The doublet pattern observed in the ^{19}F n.m.r. spectrum of the phosphorane at room temperature collapses completely at 0° and provides two broad chemically shifted regions which appear to resolve at distinctly different temperatures between -40° and -100° . At -70° the low-field component is clearly resolved into a doublet of septets (ϕ 63.7 p.p.m. vs CCl_3F , $^2J_{FF}$ 115.5, $^4J_{FF}$ 13.5 Hz) arising from coupling between non-equivalent CF_3 groups. The high-field component centred about 72 p.p.m. is complex and resolves only partially even at -100° into a doublet (J ca 108 Hz) of apparent quartets plus additional peaks spread over a region of several hundred cycles, suggesting that this part of the spectrum is second order. These spectral features become much sharper

at -140° and, in addition, the low-field doublet of septets shows additional splitting. It is clear, however, that CF_3 groups exist in two different environments at low temperatures thus excluding from the remaining two alternative trigonal-bipyramidal structures the structure in which all CF_3 groups occupy the equatorial plane of the trigonal bipyramid (II). The structure (I) seems to be the most reasonable structure in view of the evidence provided by the low temperature spectra.

The doublet pattern observed in the ^{19}F spectrum of the phosphorane at room temperature is probably due to a rapid interchanging process "pseudorotation" of the CF_3 groups. At 0° , the interchanging process has probably slowed down sufficiently so that the lifetime of any species is about the same as the n.m.r. time scale and so a collapsed doublet is observed. At -70° the interchanging process appears to be effectively quenched but now the rotational motion of one of the CF_3 groups about the P-C bond axis appears to be affected so that a complex second order ^{19}F spectrum results below this temperature. Further analysis of these n.m.r. spectra is now in progress.

CHAPTER IV

Bis(trifluoromethyl)trimethylsiloxyposphine Oxide,
 $(\text{CF}_3)_2\text{P}(\text{O})\text{OSi}(\text{CH}_3)_3$ and Bis(trifluoromethyl)trimethyl-
silylthiophosphine Sulphide, $(\text{CF}_3)_2\text{P}(\text{S})\text{SSi}(\text{CH}_3)_3$.

A variety of organic compounds of the type $\text{R}_3\text{SiOP}(\text{O})\text{R}_2$ ^{23,24,25}, $\text{R}_3\text{SiSP}(\text{S})\text{R}_2$ ²³ and $\text{R}_3\text{SiOP}(\text{S})\text{R}_2$ ²³ (where R = organic substituents) have been reported. No compounds containing $\text{P}(\text{O})\text{SSi}$ systems have however been found. Furthermore $\text{Cl}_2\text{P}(\text{O})\text{OSi}(\text{CH}_3)_3$ ²⁶ and $\text{F}_2\text{P}(\text{O})\text{OSi}(\text{CH}_3)_3$ ^{27,28} are the only compounds that have halo-substituents attached to pentavalent phosphorus atom. It is also worth mentioning that compounds of $\text{P}(\text{S})\text{SSi}$, $\text{P}(\text{S})\text{OSi}$ and $\text{P}(\text{O})\text{SSi}$ systems having fluorines or CF_3 substituents on the phosphorus atoms have not yet been reported. Herein we report the synthesis and characterization of $(\text{CF}_3)_2\text{P}(\text{O})\text{OSi}(\text{CH}_3)_3$ and $(\text{CF}_3)_2\text{P}(\text{S})\text{SSi}(\text{CH}_3)_3$ and some attempted syntheses of $\text{P}(\text{S})\text{OSi}$ systems.

1. Preparation and Characterization of Bis(trifluoro-
methyl)trimethylsiloxyposphine Oxide.

(a) From $(\text{CF}_3)_2\text{P}(\text{O})\text{Cl}$ and $[(\text{CH}_3)_3\text{Si}]_2\text{O}$

A sample of chlorobis(trifluoromethyl)phosphine oxide, $(\text{CF}_3)_2\text{P}(\text{O})\text{Cl}$ ¹⁷ (0.315 g, 1.44 mmols) was combined with $[(\text{CH}_3)_3\text{Si}]_2\text{O}$ (0.233 g, 1.44 mmols) and the reaction allowed to proceed for 41 hours at 100°.

Vacuum fractionation of the volatile products gave $(\text{CF}_3)_2\text{P}(\text{O})\text{OSi}(\text{CH}_3)_3$ (0.38 g, 1.39 mmoles), in 97% yield, which was collected at -45° , $(\text{CH}_3)_3\text{SiCl}$ (0.161 g, 1.49 mmoles) which was collected at -84° , and $(\text{CF}_3)_2\text{P}(\text{O})\text{Cl}$ (0.007 g, 0.03 mmoles) which was collected at -132° .

(b) Characterization of $(\text{CF}_3)_2\text{P}(\text{O})\text{OSi}(\text{CH}_3)_3$

The compound $(\text{CF}_3)_2\text{P}(\text{O})\text{OSi}(\text{CH}_3)_3$ is a colorless volatile liquid which was thermally stable up to 195° for extended periods of time. The vapor pressure data, given in Table III is described by the equation

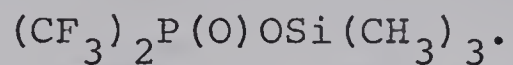
$$\log_{10} P_{\text{mm}} = +8.4216 - \frac{2241}{T}$$

which gives an extrapolated boiling point of 131.3°C , a heat of vaporization of 10256 cal/mole and a Trouton constant of 25.4 cal/mole deg.

The pure compound was further characterized by mass spectroscopy (Table IV) including accurate mass measurements of the parent ion (calcd for $(\text{CF}_3)_2\text{P}(\text{O})\text{O}^{28}\text{Si}(\text{CH}_3)_3$, m/e 274.0011; found: m/e 274.0014) by ir spectroscopy (Table V) by n.m.r. spectroscopy (Table XIV, Appendix) and by chemical reactions described below. Of further interest, the mass spectrum of $(\text{CF}_3)_2\text{P}(\text{O})\text{OSi}(\text{CH}_3)_3$ had a very strong peak at 290 (calcd for $(\text{CF}_3)_2\text{P}(\text{O})^{32}\text{Si}(\text{CH}_3)_3$ m/e 289.9785; found: m/e 289.9782) which indicated that one oxygen in

TABLE III

Observed and Calculated Vapor Pressures for



Temp. °C	Pressure, obs.	(mm) calcd.	Temp. °C	Pressure obs	(mm) calcd
4.1 ^a	2.06	2.18	45.2 ^a	24.23	24.08
10.4 ^a	3.12	3.29	49.2 ^a	29.41	29.44
15.5 ^a	4.67	4.54	53.3 ^a	36.21	36.00
19.9	6.37	5.94	56.7 ^a	42.12	42.37
22.3 ^a	7.02	6.85	56.9	42.94	42.77
25.9 ^a	8.77	8.46	59.0 ^a	46.91	47.21
30.0 ^a	11.02	10.68	65.8 ^a	64.52	64.48
34.7	13.07	13.85	71.6	82.69	83.31
38.6 ^a	17.20	17.08	74.4 ^a	93.26	93.98
42.9	20.99	21.40			

^a

Measured with descending temperatures from maximum temperature.

TABLE IV

Mass Spectrum of $(\text{CF}_3)_2\text{P}(\text{O})\text{OSi}(\text{CH}_3)_3$

m/e	$I^a, \%$	Ion^c	m/e	$I^a, \%$	Ion^c
290 ^b	0.08	$\text{C}_5\text{H}_9\text{F}_6\text{POSiS}$	141	0.13	$\text{C}_3\text{H}_9\text{FPOSi}$
275	0.06	$\text{C}_4\text{H}_6\text{F}_6\text{POSiS}$	140	0.19	
274 ^b	0.02	$\text{C}_5\text{H}_9\text{F}_6\text{PO}_2\text{Si}$	139	2.40	
260	0.11	$\text{C}_4\text{H}_6\text{F}_6\text{PO}_2\text{Si}$	137	0.06	$\text{C}_3\text{H}_7\text{FPOSi}$
259 ^b	1.16		133	0.24	CHF_3P
209	0.10	$\text{C}_3\text{H}_6\text{F}_4\text{PO}_2\text{Si}$	132	0.11	$\text{C}_2\text{F}_4\text{P}$
190	0.06	$\text{C}_3\text{H}_6\text{F}_3\text{PO}_2\text{Si}$	131	6.98	
175	0.29	$\text{C}_2\text{H}_3\text{F}_3\text{PO}_2\text{Si}$	129	0.37	$\text{CH}_4\text{F}_2\text{POSi}$
171 ^b	0.11	$\text{C}_3\text{H}_9\text{FPOSiS}$	128	0.13	$\text{CH}_3\text{F}_2\text{POSi}$
161	0.14	$\text{C}_2\text{H}_6\text{F}_2\text{PO}_2\text{Si}$	127	0.18	$\text{CH}_2\text{F}_2\text{POSi}$
160	0.27		125	0.41	$\text{C}_2\text{H}_7\text{FPOSi}$
159 ^b	3.65		121	0.56	$\text{C}_2\text{H}_3\text{FPOSi}$
156	0.06	$\text{C}_3\text{H}_9\text{FPO}_2\text{Si}$	117	0.14	$\text{C}_3\text{H}_6\text{POSi}$
155	0.76		115	0.10	$\text{H}_2\text{F}_2\text{POSi}$
151	0.06		113	0.18	F_2POSi
150	0.13	$\text{C}_5\text{H}_{15}\text{OSi}_2$	110	0.13	CH_4FPOSi
149	1.33		109	0.35	CH_3FPOSi
148	2.70		108	0.33	CH_2POSi
147 ^b	17.46	$\text{C}_2\text{H}_6\text{F}_2\text{POSi}$	107	0.08	CHFPOSi
145	0.65		105	0.13	$\text{C}_2\text{H}_6\text{POSi}$
144	1.24		103	0.22	$\text{C}_2\text{H}_4\text{POSi}$
143	17.46		101	0.10	CHF_3P

(continued.....)

TABLE IV (continued)

<u>m/e</u>	<u>I^a, %</u>	<u>Ion^c</u>	<u>m/e</u>	<u>I^a, %</u>	<u>Ion^c</u>
97	0.13	CH ₆ FPSi	80	0.08	H ₂ POSi
96	0.19		79	0.62	
95	0.25		78	0.98	
94	0.55	CH ₆ POSi	77	13.33	C ₃ H ₉ Si
93	7.46		76	0.40	
92	{ 0.18	CH ₅ POSi, CH ₃ FPSi	75	0.43	
	{ 0.11		74	0.62	C ₃ H ₈ Si
91	{ 0.32	CH ₂ FPSi, CH ₄ POSi	73	6.67	
	{ 0.73		72	1.17	C ₃ H ₇ Si
87	0.16	C ₃ H ₇ SiO	71	0.13	HF ₂ P
83	0.10	CH ₅ FPO	70	0.08	CF ₃ , F ₂ P
82	0.08	H ₃ FPSi	69	0.71	
81	1.16				

- (a) Intensities are expressed as percent total ionization defined as $\frac{I}{\sum (Int)_n}$ where n refers to all ions with $m/e > 68$ whose intensity is 0.3% of the base peak. Left hand brackets enclose reduced intensities of multiplet components at given m/e.
- (b) The identity of these peaks was established by mass measurement under high resolution.
- (c) Ions are listed only once in the Table under the most general designation.

TABLE V

Infrared Spectrum of $(\text{CF}_3)_2\text{P}(\text{O})\text{OSi}(\text{CH}_3)_3$

2973	m	$\nu(\text{C-H})$	1234 s	$\nu(\text{C-F})$	767 s	$\delta_s(\text{CF}_3)$
2914	w	$\nu(\text{C-H})$	1211 s	$\nu(\text{C-F})$	~720 vw	
2850	vw	$\nu(\text{C-H})$	1185 vs	$\nu(\text{C-F})$	665 w	
1467	w	$\delta(\text{CH}_3)$	1135 s	$\nu(\text{C-F})$	583	$\delta_a(\text{CF}_3)$
1425	w	$\delta(\text{CH}_3)$	1042 s	$\nu(\text{O-Si})$	566 m	
1333	s	$\nu(\text{P=O})$	857 s	$\nu(\text{Si-C})$	501 s	$\delta(\text{P=O})$
1266	s	$\delta(\text{Si-CH}_3)$				

s = strong, m = medium, w = weak, v = very, sh = shoulder
 ν = stretch, δ = deformation, a = antisymmetric, s = symmetric

$(\text{CF}_3)_2\text{P}(\text{O})\text{OSi}(\text{CH}_3)_3$ had been exchanged for one sulphur within the mass spectrometer.

2. Preparation and Characterization of Bis(trifluoromethyl)trimethylsilylthiophosphine Sulfide.

(a) From $(\text{CF}_3)_2\text{PS}_2\text{H}$ and $[(\text{CH}_3)_3\text{Si}]_2\text{NH}$

A sample of $(\text{CF}_3)_2\text{PS}_2\text{H}$ ²⁹ (0.195 g, 0.84 mmoles) was combined with $[(\text{CH}_3)_3\text{Si}]_2\text{NH}$ (0.068 g, 0.42 mmoles). A reaction was observed to occur immediately upon mixing of the reagents at room temperature to form a white solid and droplets of liquid. The mixed reagents were allowed to stand for 48 hours at room temperature and then the volatile products were taken into the vacuum system and separated by fractional condensation. The products obtained were $(\text{CF}_3)_2\text{P}(\text{S})\text{SSi}(\text{CH}_3)_3$ (0.066 g, 0.22 mmoles) with a trace of $[(\text{CH}_3)_3\text{Si}]_2\text{O}$ which was collected at -23° and mixtures (0.032 g) of $(\text{CF}_3)_2\text{P}(\text{S})\text{SSi}(\text{CH}_3)_3$, $(\text{CF}_3)_2\text{PS}_2\text{H}$, $(\text{CH}_3)_3\text{SiCl}$, $(\text{CF}_3)_2\text{P}(\text{O})\text{OSi}(\text{CH}_3)_3$ and other unidentified compounds (by n.m.r.) which passed the -23° trap. The n.m.r. spectrum of the white solid remaining in the reaction tube indicated the presence of the $(\text{CF}_3)_2\text{PS}_2^-$ ion.²⁰

In a second reaction, $(\text{CF}_3)_2\text{PS}_2\text{H}$ (1.284 g, 5.49 mmoles) was allowed to react with $[(\text{CH}_3)_3\text{Si}]_2\text{NH}$ (0.384 g, 2.38 mmoles) in a 75 cc reaction tube for 15 minutes at room temperature. Separation of the volatile products by fractional condensation gave $(\text{CF}_3)_2\text{P}(\text{S})\text{SSi}(\text{CH}_3)_3$

(0.811 g, 2.65 mmoles) (56% yield relative to the limiting reagent $[(\text{CH}_3)_3\text{Si}]_2\text{NH}$ which was collected at both -23° and -45° and a mixture (0.112 g) of $(\text{CF}_3)_2\text{PS}_2\text{H}$, an unidentified $(\text{CF}_3)_2\text{P}$ compound (^{19}F n.m.r. $\phi = 73.4$, $J = 116$ cps) and $[(\text{CH}_3)_3\text{Si}]_2\text{O}$ in the ratio 50:4.2:1 (by n.m.r.) which was collected at -196° . The white solid remaining in the reaction tube was not identified.

(b) Characterization of $(\text{CF}_3)_2\text{P}(\text{S})\text{SSi}(\text{CH}_3)_3$

The compound $(\text{CF}_3)_2\text{P}(\text{S})\text{SSiMe}_3$ is a colorless volatile liquid which decomposed at 100° to give $(\text{CF}_3)_2\text{P}(\text{S})\text{SP}(\text{CF}_3)_2$ and a variety of unidentified compounds. The compound was characterized by mass spectroscopy (Table VI), n.m.r. spectroscopy (Table XIV, Appendix), ir spectroscopy (Table VII) and by chemical reactions described below.

The mass spectrum gave no parent ion at 306 but a strong peak at 290 (calcd for $(\text{CF}_3)_2\text{P}^{32}(\text{S})\text{O}^{28}\text{Si}(\text{CH}_3)_3$ m/e 289.9785; found: m/e 289.9779) which may be due to a small amount of stable oxygen containing impurity in the compound which gives this prominent peak in the mass spectrum.

3. Attempted Preparation of Mixed Oxy-Thio Silane Compounds; $(\text{CF}_3)_2\text{P}(\text{S})\text{SSi}(\text{CH}_3)_3$, $(\text{CF}_3)_2\text{P}(\text{O})\text{SSi}(\text{CH}_3)_3$ and $(\text{CF}_3)_2\text{P}(\text{S})\text{OSi}(\text{CH}_3)_3$

(a) From $(\text{CF}_3)_2\text{P}(\text{S})\text{Cl}$ and $[(\text{CH}_3)_3\text{Si}]_2\text{O}$

$(\text{CF}_3)_2\text{P}(\text{S})\text{Cl}^{29}$ (0.110 g, 0.47 mmoles) and $[(\text{CH}_3)_3\text{Si}]_2\text{O}$

TABLE VI

Mass Spectrum of $(\text{CF}_3)_2\text{P}(\text{S})\text{SSi}(\text{CH}_3)_3$

m/e	I ^a , %	Ion ^b	m/e	I ^a , %	Ion ^b
292	0.03	$\text{C}_5\text{H}_9\text{F}_6\text{POSiS}$	173	0.04	$\text{C}_3\text{H}_9\text{FPOSiS}$
291	0.04		172	0.04	
290 ^c	0.32		171	0.35	
281	0.04	.	170	0.05	$\text{C}_3\text{H}_8\text{FPOSiS}$
276	0.02	$\text{C}_4\text{H}_6\text{F}_6\text{POSiS}$	165	0.16	$\text{CH}_5\text{F}_3\text{PSiS}$
275	0.16		162	0.07	$\text{CH}_2\text{F}_3\text{PSiS}$
259	0.11	$\text{C}_4\text{H}_6\text{F}_6\text{PSiS}$	159	0.03	$\text{C}_2\text{H}_6\text{F}_2\text{PSiS}$
245	0.04	$\text{C}_3\text{H}_4\text{F}_6\text{PSiS}$	155	0.09	$\text{C}_3\text{H}_9\text{FPSiS}$
241	0.05	$\text{C}_3\text{F}_6\text{PSiS}$	153	0.03	$\text{C}_2\text{H}_7\text{FPSiS}$
240	0.04	$\text{C}_4\text{H}_6\text{F}_5\text{PSiS}$	152	0.04	$\text{C}_2\text{H}_6\text{FPSiS}$
234	0.21	$\text{C}_2\text{HF}_6\text{PS}_2$	151	0.16	CF_4PS
225	0.04	$\text{C}_2\text{HF}_6\text{PSiS}$	150	0.32	$\text{C}_2\text{F}_5\text{P}$
221	0.08	$\text{C}_4\text{H}_6\text{F}_4\text{POSiS}$	149	3.12	$\text{C}_5\text{H}_{15}\text{Si}_2\text{O}$
215	0.02	$\text{C}_2\text{H}_2\text{F}_6\text{PSiS}$	148	6.49	
205	0.05	$\text{C}_3\text{H}_2\text{F}_4\text{PSiS}$	147	36.80	
204	0.02	$\text{C}_3\text{HF}_4\text{PSiS}$	146	0.03	$\text{C}_2\text{H}_3\text{F}_3\text{PSi}$
202	0.40	$\text{C}_2\text{HF}_6\text{PS}$	145	0.12	
190	0.04	$\text{C}_3\text{H}_6\text{F}_3\text{PSiS}$	144	0.20	
178	0.03	$\text{C}_2\text{H}_5\text{F}_3\text{PSiS}$	143	2.86	$\text{C}_2\text{H}_5\text{FPSiS}$
176	0.03	$\text{C}_2\text{H}_3\text{F}_3\text{PSiS}$	141	0.05	
175	0.29		140	0.05	
			139	0.47	

TABLE VI (continued)

m/e	I ^a , %	Ion ^b	m/e	I ^a , %	Ion ^b
137	0.05	C ₂ H ₃ FPSiS	106	0.03	CH ₃ PSiS
136	0.02	C ₂ H ₂ FPSiS	105	0.23	C ₃ H ₉ SiS
135	0.05	C ₂ HFPSiS	104	0.04	C ₃ H ₈ SiS
134	0.23	C ₂ FPSiS	103	0.25	C ₃ H ₇ SiS
133	{ 0.46 0.46	CHF ₃ PS	102	0.27	C ₃ H ₆ SiS
132	0.18	CF ₃ PS	101	0.36	CHF ₃ P
131	1.13	C ₂ F ₄ P	100	0.17	CF ₃ P
129	0.03	CHF ₃ PSi	97	{ 0.04 0.03	F ₂ PSi
128	0.02	CF ₃ PSi	95	0.15	CH ₅ FPSi
127	0.04	C ₂ H ₆ F ₂ PSi	94	0.06	CFPS
125	0.03	C ₂ H ₄ F ₂ PSi	93	0.48	CH ₃ FPSi
121	0.05	HF ₃ PS	92	1.34	CH ₂ FPSi
120	0.03	CHF ₄ P	91	{ 0.08 0.07	CHFPSi
119	0.09	CF ₄ P	89	0.08	C ₂ H ₅ SiS
118	0.04	H ₂ F ₃ PSi	88	0.08	C ₂ H ₄ SiS
117	0.23	HF ₃ PSi	87	0.27	C ₂ H ₃ SiS
116	0.06	C ₂ H ₄ F ₃ P	86	0.05	C ₂ H ₂ SiS
115	0.13	C ₂ H ₃ F ₃ P	85	{ 0.06 0.11	C ₂ HSiS
114	0.02	C ₂ H ₂ F ₃ P	84	0.05	C ₂ SiS
113	0.07	CF ₂ PS	83	0.80	HFPS
109	{ 0.03 0.03	CH ₆ PSiS	82	0.29	FPS
108	0.02	CH ₅ PSiS	81	0.19	CF ₂ P
107	0.02	CH ₄ PSiS	80	0.23	H ₂ FPSi

(continued.....)

TABLE VI (continued)

m/e	I ^a , %	Ion ^b	m/e	I ^a , %	Ion ^b
79	1.00	HFPSi	73	4.33	C ₃ H ₉ Si
78	1.91	FPSi	72	0.07	C ₃ H ₈ Si
77	25.76	CH ₅ SiS	71	0.12	C ₃ H ₇ Si
76	0.24	CH ₄ SiS	70	0.04	C ₃ H ₆ Si
75	0.43	CPS	69	0.07	CF ₃
74	0.39	CH ₃ PSi		1.43	

-
- (a) Intensities are expressed as percent total ionization, defined as $\frac{(Int)_n}{\sum (Int)_n}$ where n refers to all ions with $m/e > 68$ whose intensity is 0.1% of the base peak. Left hand brackets enclose reduced intensities of multiplet components at given m/e.
- (b) Ions are listed only once in the Table under the most general designation.
- (c) The identity of this peak was established by mass measurement under high resolution.

TABLE VIIInfrared Spectrum of $(\text{CF}_3)_2\text{P}(\text{S})\text{SSi}(\text{CH}_3)_3$

2931	vw	$\nu(\text{C-H})$	1163	vs	$\nu(\text{C-F})$	572 s	$\delta_a(\text{CF}_3)$
2906	vw	$\nu(\text{C-H})$	855	s	$\nu(\text{Si-C})$	526 m	$\nu(\text{P-S})$
1262	m	$\delta(\text{Si-CH}_3)$	772	m	$\delta_s(\text{CF}_3)$	477 m	$\nu(\text{P-CF}_3)$
1203	vs	$\nu(\text{C-F})$	732	s	$\nu(\text{P=S})$	429 m	
1187	vs	$\nu(\text{C-F})$	632	w			

s = strong, m = medium, w = weak, v = very, sh = shoulder,
 ν = stretch, δ = deformation, a = antisymmetric,
 s = symmetric

(0.075 g, 0.46 mmoles) did not react for 5 days at 50°, nor for 65 hours at 100°, nor for 12 days at 120°, nor for 30 days at 160°. Vacuum fractionation of the volatile products gave a mixture (0.060 g) of $[(CH_3)_3Si]_2O$ and trace of $(CF_3)_2P(S)Cl$ which was collected at -63° and a mixture (0.110 g) of $(CF_3)_2P(S)Cl$ and $[(CH_3)_3Si]_2O$ which was collected at -84°. Analysis of all the above mixtures by n.m.r. spectroscopy showed only unchanged $(CF_3)_2P(S)Cl$ and $[(CH_3)_3Si]_2O$.

(b) From $(CF_3)_2P(S)F$ and $[(CH_3)_3Si]_2S$

A sample of $(CF_3)_2P(S)F$ ²⁹ (0.256 g, 1.16 mmoles) with $[(CH_3)_3Si]_2S$ (0.246 g, 1.38 mmoles) was heated for 20 hours at 100°. The resultant pale yellowish liquid was fractionally distilled in the vacuum system to give $(CF_3)_2P(S)F$, $(CH_3)_3SiF$ and other unidentified compounds. A trace of yellow residue remained in the reaction tube. The above volatile mixtures were heated further for 4.5 days at 100°. Vacuum fractionation of the volatile products gave mixtures (0.199 g) of $(CF_3)_2PSSi(CH_3)_3$, $[(CH_3)_3Si]_2S$, and unidentified compounds (indicated by i.r.) which were collected at both -63° and -84°, and mixtures (0.266 g) of $(CF_3)_2P(S)F$, $(CH_3)_3SiF$ and unidentified compounds (indicated by i.r.) which were collected at both -116° and -196°.

(c) From $(\text{CF}_3)_2\text{P}(\text{S})\text{Cl}$ and $[(\text{CH}_3)_3\text{Si}]_2\text{S}$

$(\text{CF}_3)_2\text{P}(\text{S})\text{Cl}^{29}$ (0.201 g, 0.85 mmoles) was heated with $[(\text{CH}_3)_3\text{Si}]_2\text{S}$ (0.134 g, 0.75 mmoles) which contained a trace of $[(\text{CH}_3)_3\text{Si}]_2\text{O}$ for 39 hours at 100° . Vacuum fractionation of the volatile products gave $[(\text{CH}_3)_3\text{Si}]_2\text{S}$ (0.118 g, 0.66 mmoles) which was collected at -45° , a mixture (0.154 g) of $(\text{CF}_3)_2\text{P}(\text{S})\text{Cl}$ with traces of $[(\text{CH}_3)_3\text{Si}]_2\text{O}$ and unidentified compounds (indicated by i.r.) which was collected at -84° , and a mixture (0.048 g) of $(\text{CF}_3)_2\text{P}(\text{S})\text{Cl}$ with traces of $(\text{CH}_3)_3\text{SiCl}$ and $[(\text{CH}_3)_3\text{Si}]_2\text{O}$ which was collected at -116° . The above mixtures were heated for a further 7.5 days at 120° . Vacuum fractionation of the volatile products gave a mixture (0.114 g) of $[(\text{CH}_3)_3\text{Si}]_2\text{S}$, $[(\text{CH}_3)_3\text{Si}]_2\text{O}$, $(\text{CF}_3)_2\text{P}(\text{S})\text{SSi}(\text{CH}_3)_3$ and $(\text{CF}_3)_2\text{PSSi}(\text{CH}_3)_3$ in the ratio 25:1:1:0.7 (by n.m.r.) which was collected at -63° , mixtures (0.197 g) of $(\text{CF}_3)_2\text{P}(\text{S})\text{Cl}$, $(\text{CH}_3)_3\text{SiCl}$, $[(\text{CH}_3)_3\text{Si}]_2\text{S}$ and $[(\text{CH}_3)_3\text{Si}]_2\text{O}$ which were collected at both -84° and -116° . A reddish brown residue remained in the reaction tube.

(d) From $(\text{CF}_3)_2\text{P}(\text{S})\text{F}$ and $[(\text{CH}_3)_3\text{Si}]_2\text{O}$

A sample of $(\text{CF}_3)_2\text{P}(\text{S})\text{F}^{29}$ (0.344 g, 1.57 mmoles) was heated with $[(\text{CH}_3)_3\text{Si}]_2\text{O}$ (0.245 g, 1.57 mmoles) for 7 days at 70° . Vacuum fractionation of the volatile products gave mixtures (0.260 g) of $[(\text{CH}_3)_3\text{Si}]_2\text{O}$ and unidentified compounds which were collected at both -63° and -84° , a mixture

(0.332 g) of $(\text{CH}_3)_3\text{SiF}$ and $(\text{CF}_3)_2\text{P}(\text{S})\text{F}$ which was collected at -116° . After heating the above mixtures for a further 7 days at 100° , vacuum fractionation of the volatile products gave a mixture (0.073 g) of $(\text{CF}_3)_2\text{P}(\text{O})\text{Si}(\text{CH}_3)_3$, an unidentified compound (^{19}F n.m.r., $\phi = 73.4$, $J = 116.5$ cps) and $[(\text{CH}_3)_3\text{Si}]_2\text{O}$ in the ratio 3.3:20:1 (by n.m.r.) which was collected at -45° , mixtures (0.208 g) of $(\text{CF}_3)_2\text{P}(\text{O})\text{OSi}(\text{CH}_3)_3$, $[(\text{CH}_3)_3\text{Si}]_2\text{O}$, an unidentified compound (^{19}F n.m.r., $\phi = 73.5$, $J = 116.7$ cps) and unidentified compounds (^1H n.m.r. $\tau = 8.93, 9.26$) in the ratio 1.5:14.5: ~5.4:~1 (by n.m.r.) which were collected at both -63° and -84° and mixtures (0.205 g) of $(\text{CH}_3)_3\text{SiF}$, $(\text{CF}_3)_3\text{P}=\text{S}$, $(\text{CF}_3)_2\text{P}(\text{S})\text{F}$ and an unidentified compound (^1H n.m.r. $\tau = 8.08$) in the ratio 1.2:0.2:2.5:~1:5 (by n.m.r.) which were collected at both -116° and -196° . Ratios were calculated assuming that unknown compounds have $(\text{CF}_3)_2\text{P}$ and $(\text{CH}_3)_3\text{Si}$ structures.

(e) From $(\text{CF}_3)_2\text{P}(\text{O})\text{Cl}$ and $[(\text{CH}_3)_3\text{Si}]_2\text{S}$

A sample of $(\text{CF}_3)_2\text{P}(\text{O})\text{Cl}$ ¹⁷ (0.443 g, 2.01 mmoles) was heated with $[(\text{CH}_3)_3\text{Si}]_2\text{S}$ (0.301 g, 1.69 mmoles) for five days at 100° . Vacuum fractionation of the volatile products gave a mixture (0.358 g) of $[(\text{CH}_3)_3\text{Si}]_2\text{S}$, $(\text{CF}_3)_2\text{P}(\text{O})\text{OSi}(\text{CH}_3)_3$ and an unidentified $(\text{CF}_3)_2\text{P}$ compound (^{19}F : $\phi = 73.4$, $J = 116$ cps) in the ratio 9:3:5 (by n.m.r.) which was collected at -63° and a mixture (0.372 g) of $(\text{CH}_3)_3\text{SiCl}$, $(\text{CF}_3)_2\text{P}(\text{O})\text{Cl}$ and unidentified compounds (indicated by i.r.) which was collected at -116° .

(f) From $(\text{CF}_3)_2\text{PS}_2\text{H}$ and $[(\text{CH}_3)_3\text{Si}]_2\text{O}$

A sample of $(\text{CF}_3)_2\text{PS}_2\text{H}$ ²⁹ (0.250 g, 1.07 mmoles) was heated with $[(\text{CH}_3)_3\text{Si}]_2\text{O}$ (0.143 g, 0.88 mmoles) for 7 days at 70°. Vacuum fractionation of the volatile products gave a mixture (0.347 g) of $(\text{CF}_3)_2\text{PS}_2\text{H}$, $[(\text{CH}_3)_3\text{Si}]_2\text{O}$ with traces of $(\text{CF}_3)_2\text{P}(\text{S})\text{SSi}(\text{CH}_3)_3$ and unidentified compounds which was collected at -63° and a mixture (0.011 g) of $(\text{CH}_3)_3\text{SiF}$, $[(\text{CH}_3)_3\text{Si}]_2\text{O}$ and an unidentified compound which was collected at -196°.

(g) From $(\text{CF}_3)_2\text{P}(\text{S})\text{SSi}(\text{CH}_3)_3$ and $[(\text{CH}_3)_3\text{Si}]_2\text{O}$

A sample of $(\text{CF}_3)_2\text{P}(\text{S})\text{SSi}(\text{CH}_3)_3$ was heated with $[(\text{CH}_3)_3\text{Si}]_2\text{O}$ for 37 hours at 100°. The reaction mixture was analysed by n.m.r. spectroscopy and it gave $[(\text{CH}_3)_3\text{Si}]_2\text{O}$, $(\text{CF}_3)_2\text{PS}_2\text{H}$, $(\text{CF}_3)_2\text{P}(\text{S})\text{SSi}(\text{CH}_3)_3$ and traces of unidentified compounds in the ratio 24:7:1: > 0.5 (by n.m.r.). A brownish residue remained in the reaction tube.

4. Reactions of $(\text{CF}_3)_2\text{P}(\text{O})\text{OSi}(\text{CH}_3)_3$ (a) With Water

A sample of $(\text{CF}_3)_2\text{P}(\text{O})\text{OSi}(\text{CH}_3)_3$ (0.086 g, 0.31 mmoles) was allowed to react with 1 cc of H_2O for 4 days at room temperature. Vacuum fractionation of the volatile products gave only $[(\text{CH}_3)_3\text{Si}]_2\text{O}$ (0.026 g, 0.16 mmoles) which was collected at -84°. Neutralization

of the aqueous solution with sodium hydroxide gave a solution containing the $(\text{CF}_3)_2\text{PO}_2^-$ ion according to the n.m.r.²⁰

(b) Alkaline Hydrolysis

A sample of $(\text{CF}_3)_2\text{P}(\text{O})\text{OSi}(\text{CH}_3)_3$ (0.091 g, 0.33 mmoles) was treated with excess degassed 10% NaOH solution for 7 days at room temperature. The volatile products were $[(\text{CH}_3)_3\text{Si}]_2\text{O}$ (0.024 g, 0.15 mmoles) which was collected at -132° , and CF_3H (0.024 g, 0.34 mmoles) which was collected at -196° . The n.m.r. spectrum²⁰ of the remaining aqueous solution indicated the presence of the $\text{CF}_3\text{PO}_3^{=}$ ion.

(c) With Dimethylamine

$(\text{CF}_3)_2\text{P}(\text{O})\text{OSi}(\text{CH}_3)_3$ (0.069 g, 0.25 mmoles) and $(\text{CH}_3)_2\text{NH}$ (0.036 g, 0.80 mmoles) were allowed to react for 9 days at room temperature. Vacuum fractionation of the volatile products gave $(\text{CH}_3)_3\text{SiN}(\text{CH}_3)_2$ (0.028 g, 0.24 mmoles) which was collected at -84° and $(\text{CH}_3)_2\text{NH}$ (0.014 g, 0.31 mmoles) which was collected at -116° . The n.m.r. spectrum²⁰ of the residual white solid dissolved in CD_3CN indicated the presence of $(\text{CF}_3)_2\text{PO}_2^- \text{H}_2^+\text{N}(\text{CH}_3)_2$.

(d) Pyrolysis

A sample of $(\text{CF}_3)_2\text{P}(\text{O})\text{OSi}(\text{CH}_3)_3$ (0.079 g, 0.29

mmoles) heated for 15 days at 195° was quantitatively recovered (0.078 g, 0.29 mmoles). N.m.r. spectroscopy of the recovered sample showed only $(\text{CF}_3)_2\text{P}(\text{O})\text{OSi}(\text{CH}_3)_3$.

(e) With Anhydrous HCl

A sample of $(\text{CF}_3)_2\text{P}(\text{O})\text{OSi}(\text{CH}_3)_3$ (0.116 g, 0.42 mmoles) was allowed to react with HCl (0.048 g, 1.33 mmoles) for 4 days at room temperature. Vacuum fractionation of the volatile products gave a mixture (0.076 g) of $(\text{CF}_3)_2\text{P}(\text{O})\text{OSi}(\text{CH}_3)_3$ and $[(\text{CH}_3)_3\text{Si}]_2\text{O}$ in the ratio 50:1 plus traces (by n.m.r.) of unidentified compounds (^1H , $\tau = 9.70$; ^{19}F , $\phi = 70$, singlet) all collected at -63° , a mixture (0.028 g) of $(\text{CF}_3)_2\text{P}(\text{O})\text{OSi}(\text{CH}_3)_3$ and $(\text{CH}_3)_3\text{SiCl}$ in the ratio 1.6:1 (by n.m.r.) which was collected at -116° and a mixture (0.042 g) of HCl and traces of unidentified compounds (indicated by i.r.) which was collected at -196° .

5. Reactions of $(\text{CF}_3)_2\text{P}(\text{S})\text{Si}(\text{CH}_3)_3$

(a) With Water

A sample of $(\text{CF}_3)_2\text{P}(\text{S})\text{Si}(\text{CH}_3)_3$ (0.042 g, 0.14 mmoles) was combined with an excess of distilled H_2O for 3 days at room temperature. Vacuum fractionation of the volatile products gave $[(\text{CH}_3)_3\text{Si}]_2\text{O}$ (0.008 g, 0.05 mmoles) and traces of unidentified impurities. The n.m.r. spectrum of the solution remaining in the reaction

tube indicated the presence of the $(\text{CF}_3)_2\text{PS}_2^-$ ion.²⁰

(b) Alkaline Hydrolysis

$(\text{CF}_3)_2\text{P}(\text{S})\text{SSi}(\text{CH}_3)_3$ (0.077 g, 0.25 mmoles) was treated with a 10% NaOH solution for 14 hours at room temperature. Vacuum fractionation of the volatile products gave $[(\text{CH}_3)_3\text{Si}]_2\text{O}$ (0.017 g, 0.11 mmoles) which was collected at -84° and CF_3H (0.018 g, 0.26 mmoles) (found $M = 72$, calcd for $\text{CF}_3\text{H}:M = 70$) which was collected at -196° . The n.m.r. spectrum of the solution remaining in the reaction tube indicated the presence of the $\text{CF}_3\text{PS}_2\text{O}^-$ ion.²⁰

(c) With Dimethylamine

$(\text{CF}_3)_2\text{P}(\text{S})\text{SSi}(\text{CH}_3)_3$ (0.099 g, 0.32 mmoles) was allowed to react with $(\text{CH}_3)_2\text{NH}$ (0.042 g, 0.93 mmoles) for 2 days at room temperature. Vacuum fractionation of the volatile products gave mixtures (0.033 g) of $(\text{CH}_3)_3\text{SiN}(\text{CH}_3)_2$ and $[(\text{CH}_3)_3\text{Si}]_2\text{O}$ (possibly due to trace of H_2O) in the ratio 7.1:1 (by n.m.r.) which were collected at both -84° and -116° and another mixture (0.007 g) of $(\text{CH}_3)_2\text{NH}$ and trace of $(\text{CH}_3)_3\text{SiN}(\text{CH}_3)_2$ which was collected at -196° . The n.m.r. spectrum²⁰ of the remaining involatile liquid indicated the presence of the $(\text{CF}_3)_2\text{PS}_2^-\text{H}_2\text{N}(\text{CH}_3)_2^+$ salt.

(d) Pyrolysis

A sample of $(\text{CF}_3)_2\text{P}(\text{S})\text{SSi}(\text{CH}_3)_3$ (0.073 g, 0.24 mmoles)

was heated for 69 hours at 100°. The liquid contained in the tube after this treatment was a pale yellow color. The total weight (0.054 g) of the volatile product recovered was found to contain a variety of products as indicated in the following list. Identifications are made where possible. A white residue remained in the reaction tube.

^1H		^{19}F				Identity
τ	h (cm)	ϕ	J (cps)	h^b (cm)	App ^a	
9.27	1.9	71.5	106	9.3	c	$(\text{CF}_3)_2\text{P}(\text{S})\text{SSi}(\text{CH}_3)_3$
9.70	0.3	-	-	-	-	?
9.82	0.3	-	-	-	-	?
9.90	0.2	-	-	-	-	?
		53.7	81	0.8	c	$(\text{CF}_3)_2\text{P}(\text{S})\text{SP}(\text{CF}_3)_2$
		68.6	112	0.8	d	
		62.9	105	0.2	c	?
		73.3	118	0.3	c	?

^a Appearance of spectrum due to spin-spin splitting pattern.

^b Total integrated intensity of spin splitting pattern.

^c Doublet

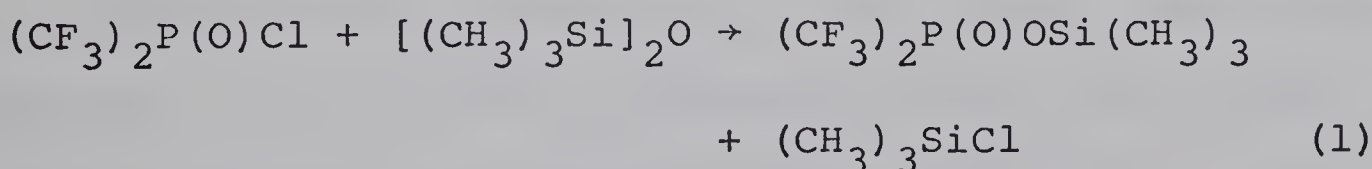
^d Doublet of doublet

(e) With Anhydrous HCl

A sample of $(\text{CF}_3)_2\text{P}(\text{S})\text{Si}(\text{CH}_3)_3$ (0.060 g, 0.20 mmoles) was allowed to react with excess HCl for 54 hours at room temperature. Vacuum fractionation of the volatile products gave mixtures (0.053 g) of $(\text{CF}_3)_2\text{PS}_2\text{H}$, $(\text{CH}_3)_3\text{SiCl}$ and $[(\text{CH}_3)_3\text{Si}]_2\text{O}$ in the ratio 20:18:1 (by n.m.r.) which were collected at both -84° and -116° with the unreacted HCl recovered in the most volatile fraction.

6. Results and Discussions

The reaction of $(\text{CF}_3)_2\text{P}(\text{O})\text{Cl}$ with $[(\text{CH}_3)_3\text{Si}]_2\text{O}$ at 100° gave $(\text{CF}_3)_2\text{P}(\text{O})\text{OSi}(\text{CH}_3)_3$ almost quantitatively according to equation (1).



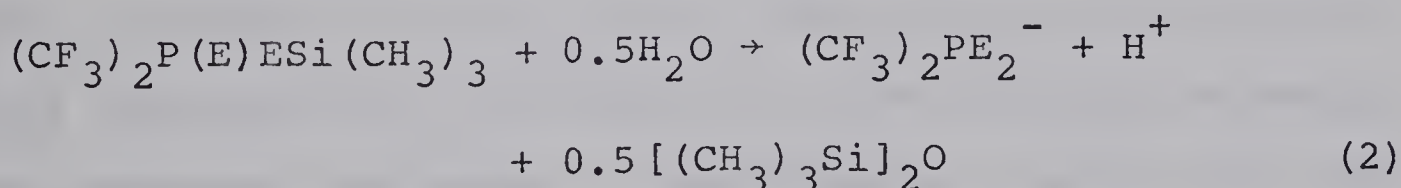
In contrast, $(\text{CF}_3)_2\text{P}(\text{S})\text{Si}(\text{CH}_3)_3$ could not be prepared from $(\text{CF}_3)_2\text{P}(\text{S})\text{X}$ ($\text{X} = \text{F}, \text{Cl}$) and $[(\text{CH}_3)_3\text{Si}]_2\text{S}$. Heating $(\text{CF}_3)_2\text{P}(\text{S})\text{Cl}$ with $[(\text{CH}_3)_3\text{Si}]_2\text{S}$ for several days at 120° gave only a trace of the desired $(\text{CF}_3)_2\text{P}(\text{S})\text{Si}(\text{CH}_3)_3$ and some $(\text{CF}_3)_2\text{PSSi}(\text{CH}_3)_3$. Similarly when $(\text{CF}_3)_2\text{P}(\text{S})\text{F}$ was heated with $[(\text{CH}_3)_3\text{Si}]_2\text{S}$ at 100° , only traces of $(\text{CF}_3)_2\text{PSSi}(\text{CH}_3)_3$, $(\text{CH}_3)_3\text{SiF}$ and unidentified compounds were found. A pure sample of $(\text{CF}_3)_2\text{P}(\text{S})\text{Si}(\text{CH}_3)_3$ suffered about 25% decomposition at 100° to give $(\text{CF}_3)_2\text{P}(\text{S})\text{SP}(\text{CF}_3)_2$ and unidentified compounds. The thermal decomposition

further complicates the synthesis of $(\text{CF}_3)_2\text{P}(\text{S})\text{SSi}(\text{CH}_3)_3$ by these high temperature methods. It was found that the desired compound $(\text{CF}_3)_2\text{P}(\text{S})\text{SSi}(\text{CH}_3)_3$ could be prepared at room temperature from the reaction of the strong acid $(\text{CF}_3)_2\text{PS}_2\text{H}$ with $[(\text{CH}_3)_3\text{Si}]_2\text{NH}$ for 15 minutes. The yield was about 56% relative to the initial amount of $[(\text{CH}_3)_3\text{Si}]_2\text{NH}$ taken. Some $[(\text{CH}_3)_3\text{Si}]_2\text{O}$ was found which probably came from the reaction of $[(\text{CH}_3)_3\text{Si}]_2\text{NH}$ with traces of water.² The white salt remained in the reaction tube which was not thoroughly investigated but it was most likely $(\text{CF}_3)_2\text{P}(\text{S})\text{S}^- \text{NH}_4^+$, since the $(\text{CH}_3)_3\text{SiNH}_3^+$ ion has not been prepared. According to Eaborn,³⁰ $(\text{C}_2\text{H}_5)_3\text{SiNH}_2$ reacted with HX to give only $(\text{C}_2\text{H}_5)_3\text{SiX}$ and NH_4X salt.

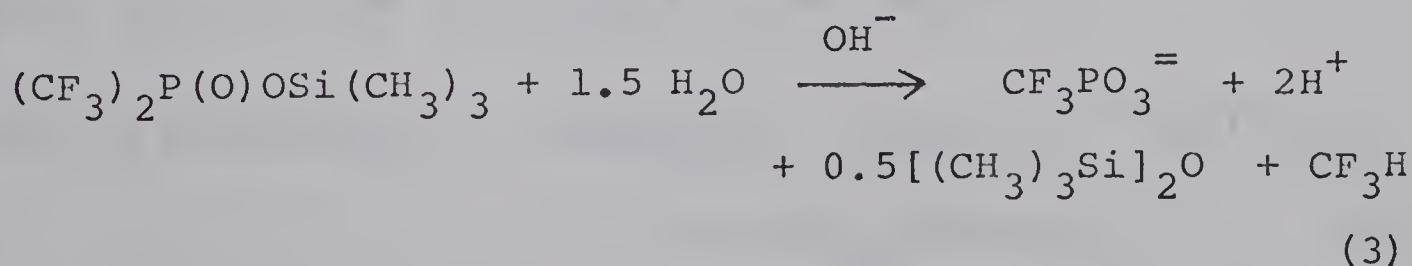
Although the $\text{R}_2\text{P}(\text{S})\text{OSiR}_3$ ²³ ($\text{R} = \text{alkyl}$) have been reported, no $\text{R}_2\text{P}(\text{O})\text{SSiR}_3$ compounds have yet been made. Several attempts to synthesize $(\text{CF}_3)_2\text{P}(\text{S})\text{OSi}(\text{CH}_3)_3$ and $(\text{CF}_3)_2\text{P}(\text{O})\text{SSi}(\text{CH}_3)_3$ were made. Reaction of $(\text{CF}_3)_2\text{P}(\text{S})\text{F}$ with $[(\text{CH}_3)_3\text{Si}]_2\text{O}$ at 100° for several days gave only a trace of $(\text{CF}_3)_2\text{P}(\text{O})\text{OSi}(\text{CH}_3)_3$. No reaction took place between $(\text{CF}_3)_2\text{P}(\text{S})\text{Cl}$ and $[(\text{CH}_3)_3\text{Si}]_2\text{O}$ at 100° . When $(\text{CF}_3)_2\text{P}(\text{O})\text{Cl}$ was heated with $[(\text{CH}_3)_3\text{Si}]_2\text{S}$ for several days at 100° , only a trace of $(\text{CF}_3)_2\text{P}(\text{O})\text{OSi}(\text{CH}_3)_3$ and unidentified compounds were found. Furthermore when $(\text{CF}_3)_2\text{PS}_2\text{H}$ was heated with $[(\text{CH}_3)_3\text{Si}]_2\text{O}$ at 70° , only a trace of $(\text{CF}_3)_2\text{P}(\text{S})\text{SSi}(\text{CH}_3)_3$ and $(\text{CH}_3)_3\text{SiF}$ was found.

Finally when $(\text{CF}_3)_2\text{P}(\text{S})\text{SSi}(\text{CH}_3)_3$ was heated with $[(\text{CH}_3)_3\text{Si}]_2\text{O}$ at 100° , some $(\text{CF}_3)_2\text{PS}_2\text{H}$, small amount of recovered $(\text{CF}_3)_2\text{P}(\text{S})\text{SSi}(\text{CH}_3)_3$ and unidentified compounds were found. It seems that the compounds $(\text{CF}_3)_2\text{P}(\text{O})\text{SSi}(\text{CH}_3)_3$ and $(\text{CF}_3)_2\text{P}(\text{S})\text{OSi}(\text{CH}_3)_3$ are not easily obtained and therefore alternate methods probably involving conditions of lower temperature should be attempted.

The chemical behavior of $(\text{CF}_3)_2\text{P}(\text{E})\text{ESi}(\text{CH}_3)_3$ ($\text{E} = \text{O}, \text{S}$) is typical of that of a bistrifluoromethyl phosphorus compound containing a pentavalent tetracoordinated phosphorus atom. The compounds $(\text{CF}_3)_2\text{P}(\text{E})\text{ESi}(\text{CH}_3)_3$ ($\text{E} = \text{O}, \text{S}$) reacted with water to give a one-half molar equivalent of $[(\text{CH}_3)_3\text{Si}]_2\text{O}$ and one molar equivalent of the $(\text{CF}_3)_2\text{PE}_2^-$ ion according to eqn (2).

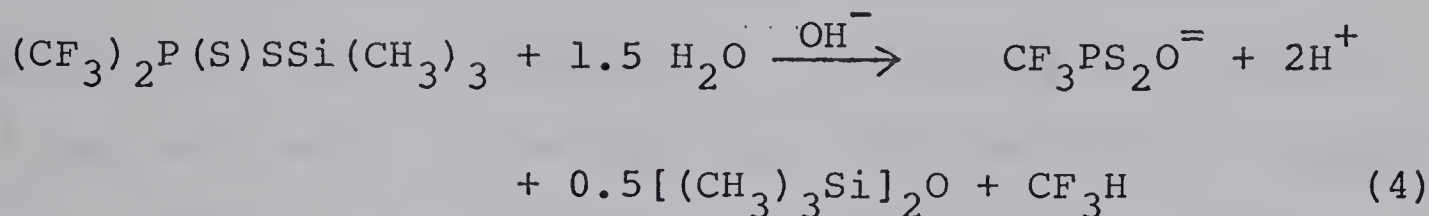


Futhermore alkaline hydrolysis of $(\text{CF}_3)_2\text{P}(\text{O})\text{OSi}(\text{CH}_3)_3$ gave $[(\text{CH}_3)_3\text{Si}]_2\text{O}$, CF_3H and the CF_3PO_3^- ion according to eqn (3).



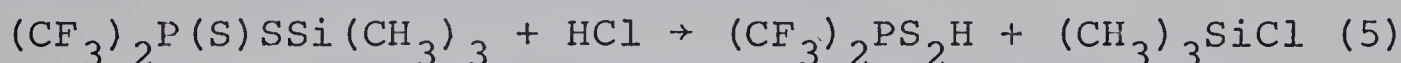
Similarly alkaline hydrolysis of $(\text{CF}_3)_2\text{P}(\text{S})\text{SSi}(\text{CH}_3)_3$ gave

$[(\text{CH}_3)_3\text{Si}]_2\text{O}$, CF_3H and the $\text{CF}_3\text{PS}_2\text{O}^-$ ion according to eqn (4).

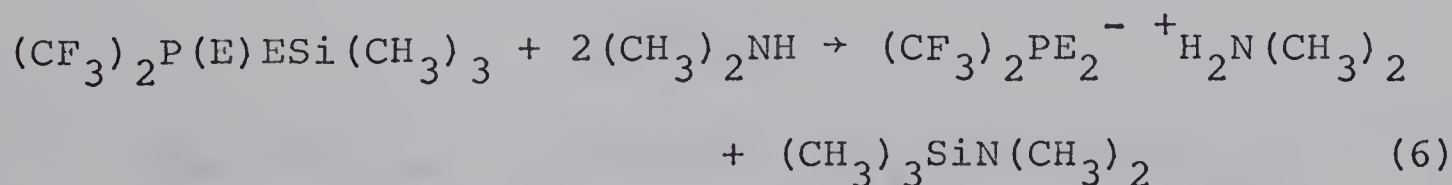


All of these reactions are typical of the four coordinate pentavalent bistrifluoromethyl phosphorus compounds.²⁰

Molar quantities of anhydrous HCl reacted with $(\text{CF}_3)_2\text{P}(\text{S})\text{SSi}(\text{CH}_3)_3$ to give $(\text{CF}_3)_2\text{PS}_2\text{H}$ and $(\text{CH}_3)_3\text{SiCl}$ in nearly quantitative yields according to eqn (5).



In contrast the reaction of $(\text{CF}_3)_2\text{P}(\text{O})\text{OSi}(\text{CH}_3)_3$ with HCl gave a mixture of $(\text{CH}_3)_3\text{SiCl}$, $[(\text{CH}_3)_3\text{Si}]_2\text{O}$ and unidentified compounds but the majority of the starting material was recovered unchanged. Dimethylamine reacted with the $(\text{CF}_3)_2\text{P}(\text{E})\text{ESi}(\text{CH}_3)_3$ ($\text{E} = \text{O}, \text{S}$) compounds to give nearly quantitative yield of $(\text{CH}_3)_3\text{SiN}(\text{CH}_3)_2$ and a white salt which was identified (by n.m.r. spectrum) as the dimethylamine salt of the $(\text{CF}_3)_2\text{PE}_2\text{H}$ acids (eqn (6)).



It seems reasonable to suggest that the reaction of these

protonic reagents involves attack at the silicon atom by the nucleophilic nitrogen or chlorine atoms in dimethylamine or HCl. With dimethylamine formation of the initial adduct with $(\text{CF}_3)_2\text{P}(\text{E})\text{ESi}(\text{CH}_3)_3$ is followed by cleavage of the E-Si bond to give the acid $(\text{CF}_3)_2\text{PE}_2\text{H}$ which further reacts with a second mole of $(\text{CH}_3)_2\text{NH}$ to give a salt. Similarly for the HCl reaction, the chlorine atom probably attacks at the silicon atom followed by cleavage of the E-Si bond to give $(\text{CH}_3)_3\text{SiCl}$. The very small amount of reaction in the case when $(\text{CF}_3)_2\text{P}(\text{O})\text{OSi}(\text{CH}_3)_3$ was treated with HCl may be due to stronger Si-O bond enhanced by some π bonding in the P-O-Si bridge system.

7. Structures of the Pentavalent Phosphino Silanes

The results of n.m.r. and i.r. spectroscopy support the pentavalent, tetracoordinated phosphorus structure shown in Figure 4 which is in agreement with the chemical behavior.

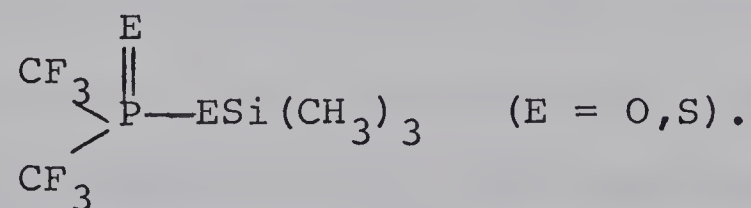


FIGURE 4

The ^{19}F n.m.r. spectra of $(\text{CF}_3)_2\text{P}(\text{E})\text{ESi}(\text{CH}_3)_3$ ($\text{E} = \text{O}, \text{S}$) showed chemical shifts and coupling constants

(Table XIV, Appendix) that are characteristic of penta-valent, tetracoordinated phosphorus atom.^{31,32} In addition the ^{31}P n.m.r. spectra of $(\text{CF}_3)_2\text{P}(\text{E})\text{ESi}(\text{CH}_3)_3$ showed in each case the characteristic seven line patterns (Table XIV, Appendix) with an intensity distribution in good agreement with that calculated for the septet due to the coupling of six equivalent fluorine atoms thus confirming the presence of two CF_3 groups on phosphorus atom.

Additional confirmation of the structures is given by i.r. spectra. In the case of $(\text{CF}_3)_2\text{P}(\text{O})\text{OSi}(\text{CH}_3)_3$, strong bands at 1333 cm^{-1} and 501 cm^{-1} can be assigned to $\text{P}=\text{O}$ stretching and bending frequencies respectively being in good agreement with those bands observed in $(\text{CF}_3)_3\text{P}=\text{O}$ and $(\text{CF}_3)_2\text{P}(\text{O})\text{Cl}$ (1327 cm^{-1} , 500 cm^{-1} and 1332 cm^{-1} , 504 cm^{-1} respectively).²² Another band at 1042 cm^{-1} was assigned to $\text{O}-\text{Si}$ stretching frequency being similar to the stretching bands of methylpolysiloxanes (1052 cm^{-1}).³³ Also in the case of $(\text{CF}_3)_2\text{P}(\text{S})\text{SSi}(\text{CH}_3)_3$, a strong band at 732 cm^{-1} can be reasonably be assigned to $\text{P}=\text{S}$ stretching frequency since $\text{P}=\text{S}$ stretching in $(\text{CF}_3)_2\text{P}(\text{S})\text{Cl}$ and $(\text{CF}_3)_2\text{P}(\text{S})\text{SCH}_3$ were found at 732 cm^{-1} and 796 cm^{-1} respectively.³⁴ Finally $\text{P}-\text{S}$ stretching frequency in $(\text{CF}_3)_2\text{P}(\text{S})\text{SSi}(\text{CH}_3)_3$ is assigned to a medium band at 526 cm^{-1} which is in fair agreement with those of $(\text{CF}_3)_2\text{P}(\text{S})\text{SCH}_3$ and $(\text{CF}_3)_2\text{P}(\text{S})\text{SH}$ (518 cm^{-1} and 524 cm^{-1} respectively).³⁴

CHAPTER V

Bis(trifluoromethyl)trimethylsiloxylphosphine,

$(\text{CF}_3)_2\text{POSi}(\text{CH}_3)_3$ and Bis(trifluoromethyl)trimethylsilyl-
thiophosphine, $(\text{CF}_3)_2\text{PSSi}(\text{CH}_3)_3$.

Although several tervalent organic phosphorus compounds containing a POSi bridge have been reported^{35,36} no PSSi bridge compounds have been found. The only reported fluorophosphorus $\text{P}^{\text{III}}\text{OSi}$ bridge compounds are $(\text{CF}_3)_2\text{POSiH}_3$, $(\text{CF}_3)_2\text{POSi}(\text{CH}_3)_3$, $[(\text{CF}_3)_2\text{PO}]_3\text{SiH}$ and $[(\text{CF}_3)_2\text{PO}]_4\text{Si}$.³⁷

We describe in this Chapter the preparation and some chemical and physical properties of bis(trifluoromethyl)trimethylsiloxylphosphine $(\text{CF}_3)_2\text{POSi}(\text{CH}_3)_3$ and bis(trifluoromethyl)trimethylsilylthiophosphine, $(\text{CF}_3)_2\text{PSSi}(\text{CH}_3)_3$.

1. Preparation of Bis(trifluoromethyl)trimethylsiloxyl- phosphine, $(\text{CF}_3)_2\text{POSi}(\text{CH}_3)_3$

(a) From $(\text{CF}_3)_2\text{PF}$ and $[(\text{CH}_3)_3\text{Si}]_2\text{O}$

A sample of $(\text{CF}_3)_2\text{PF}^{38}$ (0.086 g, 0.46 mmoles) was heated with $[(\text{CH}_3)_3\text{Si}]_2\text{O}$ (0.073 g, 0.45 mmoles) for 4 days at 100° . Vacuum fractionation of the volatile products gave $(\text{CF}_3)_2\text{POSi}(\text{CH}_3)_3$ (0.108 g, 0.42 mmoles) containing a trace of $[(\text{CF}_3)_2\text{P}]_2\text{O}$ collected at both -63° and -84° , a mixture (0.043 g) (found M, 107) of $(\text{CH}_3)_3\text{SiF}$ and a trace of unidentified compounds which was

collected at -132° and some unreacted $(\text{CF}_3)_2\text{PF}$ (0.003 g, 0.02 mmoles) which was collected at -196° .

(b) From $(\text{CF}_3)_2\text{PCl}$ and $[(\text{CH}_3)_3\text{Si}]_2\text{O}$

A sample of $(\text{CF}_3)_2\text{PCl}^{39}$ (0.151 g, 0.93 mmoles) was allowed to react with $[(\text{CH}_3)_3\text{Si}]_2\text{O}$ (0.212 g, 1.04 mmoles) for 7 days at 100° . Vacuum fractionation of the volatile products gave mixtures (0.161 g) of $[(\text{CH}_3)_3\text{Si}]_2\text{O}$ and $(\text{CF}_3)_2\text{POSi}(\text{CH}_3)_3$ which were collected at both -63° and -84° and mixtures (0.211 g) of $(\text{CF}_3)_2\text{PCl}$ and trace of $(\text{CH}_3)_3\text{SiCl}$ which were collected at both -116° and -196° . The reaction mixtures were recombined and heated for a further 8 days at 160° . Vacuum fractionation of the volatile products obtained at the end of this treatment yielded mixtures (0.157 g) of $[(\text{CH}_3)_3\text{Si}]_2\text{O}$ and $(\text{CF}_3)_2\text{POSi}(\text{CH}_3)_3$ in the ratio 8.5:1 (by n.m.r.) which were collected at both -63° and -84° and another mixture (0.199 g) of $(\text{CF}_3)_2\text{PCl}$ and trace of $(\text{CH}_3)_3\text{SiCl}$ which was collected at -116° .

2. Preparation of Bis(trifluoromethyl)trimethylsilylthio-
phosphine, $(\text{CF}_3)_2\text{PSSi}(\text{CH}_3)_3$.

(a) From $(\text{CF}_3)_2\text{PCl}$ and $[(\text{CH}_3)_3\text{Si}]_2\text{S}$

A quantity of $(\text{CF}_3)_2\text{PCl}^{39}$ (0.603 g, 2.95 mmoles) [containing a trace of $(\text{CF}_3)_3\text{P}$ (~ 0.018 g)] was heated with

$[(\text{CH}_3)_3\text{Si}]_2\text{S}$ (0.477 g, 2.68 mmoles) for 7 days at 100° . Vacuum fractionation of the volatile products gave a mixture (0.754 g) of $(\text{CF}_3)_2\text{PSSi}(\text{CH}_3)_3$ and $[(\text{CF}_3)_2\text{P}]_2\text{S}$ which was collected at -63° , a mixture (0.309 g) of $(\text{CH}_3)_3\text{SiCl}$ and $[(\text{CF}_3)_2\text{P}]_2\text{S}$ which was collected at -84° and mixtures (0.045 g) of $(\text{CF}_3)_3\text{P}$ and $(\text{CH}_3)_3\text{SiCl}$ which were collected at both -116° and -196° .

Separation of the above mixtures with the Leroy still gave $(\text{CH}_3)_3\text{SiCl}$ (0.310 g, 2.87 mmoles) (found M, 112; calcd for $(\text{CH}_3)_3\text{SiCl}$ M, 108), $(\text{CF}_3)_3\text{P}$ (0.018 g) [contaminated with a trace of $(\text{CF}_3)_2\text{PCl}$], $(\text{CF}_3)_2\text{PSSi}(\text{CH}_3)_3$ (0.602 g, 2.20 mmoles), $[(\text{CF}_3)_2\text{P}]_2\text{S}$ (0.111 g, 0.30 mmoles) and an unseparated mixture (0.024 g) of $[(\text{CF}_3)_2\text{P}]_2\text{S}$ and $(\text{CH}_3)_3\text{SiCl}$.

3. Characterization of Bis(trifluoromethyl)trimethylsiloxyposphine and Bis(trifluoromethyl)trimethylsilylthiophosphine.

The compounds, $(\text{CF}_3)_2\text{POSi}(\text{CH}_3)_3$ and $(\text{CF}_3)_2\text{PSSi}(\text{CH}_3)_3$, are clear, colorless, volatile liquids. The oxy-silane $(\text{CF}_3)_2\text{POSi}(\text{CH}_3)_3$ was thermally stable up to 195° for extended periods of time but about 10% of a sample of $(\text{CF}_3)_2\text{PSSi}(\text{CH}_3)_3$ had decomposed after heating to 195° for 9 days to give $[(\text{CF}_3)_2\text{P}]_2\text{S}$, $[(\text{CH}_3)_3\text{Si}]_2\text{S}$, $[(\text{CH}_3)_3\text{Si}]_2$, $(\text{CH}_3)_3\text{SiF}$ and several unidentified compounds. The pyrolysis results are given in more detail in section 5(e) below.

The compounds were further characterized by their spectroscopic properties (i.r., Table VIII, IX, and n.m.r. Table XIV, Appendix), by mass spectroscopy (Table X and XI) including accurate mass measurements of the parent ions (calcd for $(\text{CF}_3)_2\text{POSi}^{28}(\text{CH}_3)_3$, m/e 258.0064; found: m/e 258.0060; calcd for $(\text{CF}_3)_2\text{P}^{32}\text{S}^{28}\text{Si}(\text{CH}_3)_3$, m/e 273.9836; found: m/e 273.9838) and by the chemical reactions described below.

4. Reactions of $(\text{CF}_3)_2\text{POSi}(\text{CH}_3)_3$

(a) With Water

$(\text{CF}_3)_2\text{POSi}(\text{CH}_3)_3$ (0.054 g, 0.21 mmoles) was contained with an excess of degassed H_2O and allowed to react at room temperature for 2 days. Fractional condensation of the volatile products in vacuum gave $[(\text{CH}_3)_3\text{Si}]_2\text{O}$ (0.016 g, 0.10 mmoles) which was collected at -84° and CF_3H (0.014 g, 0.20 mmoles) (found M, 74; calcd for CF_3H : M, 70) which was collected at -196° . The n.m.r. spectrum of the solution remaining in the reaction tube indicated the presence of the $\text{CF}_3\text{P}(\text{H})\text{O}_2^-$ ion.²⁰

(b) Alkaline Hydrolysis

$(\text{CF}_3)_2\text{POSi}(\text{CH}_3)_3$ (0.066 g, 0.26 mmoles) was combined with 1 cc of 20% NaOH solution and allowed to react for 24 hours at room temperature. Vacuum fractionation of the volatile products gave $[(\text{CH}_3)_3\text{Si}]_2\text{O}$ (0.019 g, 0.12 mmoles) which was collected at -84° and CF_3H (0.037 g, 0.53 mmoles)

TABLE VIIIInfrared Spectrum of $(\text{CF}_3)_2\text{POSi}(\text{CH}_3)_3$ ^a

2966	s	$\nu_a(\text{C-H})$	1174	vs	$\nu(\text{C-F})$
2908	w	$\nu_a(\text{C-H})$	1149	vs	$\nu(\text{C-F})$
2270	vw		1109	vs	$\nu(\text{C-F})$
2240	vw	.	1052	m	$\nu(\text{Si-O})$
1965	vw		996	vs	$\nu(\text{P-O})$
1666	vw		858	vs	$\nu(\text{Si-C})$
1470	w		764	m	$\delta_s(\text{CF}_3)$
1463	w		676	w	
1452	w		668	w-sh	
1421	w		607	w	
1268	s	$\delta(\text{Si-CH}_3)$	557	m	$\delta_a(\text{CF}_3)$
1224	vs	$\nu(\text{C-F})$	554	w-sh	
1200	m-sh		457	s	$\nu(\text{P-CF}_3)$

s = strong, m = medium, w = weak, v = very, sh = shoulder
 ν = stretch, δ = deformation, a = antisymmetric, s = symmetric.

(a) Infrared spectrum is in agreement with Burg and Basi's spectrum.³⁷

TABLE IX

Infrared Spectrum of $(\text{CF}_3)_2\text{PSSi}(\text{CH}_3)_3$ ^a

2980	w-sh	$\nu(\text{C-H})$	761	w	$\delta_s(\text{CF}_3)$
2965	w	$\nu(\text{C-H})$	749	vw	
2908	vw	$\nu(\text{C-H})$	700	vw	
1415	vw		633	w	
1262	m	$\delta(\text{Si-CH}_3)$	559	w	$\delta_a(\text{CF}_3)$
1200	vs	$\nu(\text{C-F})$	527	w	$\nu(\text{P-S})$
1163	vs	$\nu(\text{C-F})$	457	w	
1127	vs	$\nu(\text{C-F})$	447	w	$\nu(\text{P-CF}_3)$
850	s	$\nu(\text{Si-C})$			

s = strong, m = medium, w = weak, v = very, sh = shoulder
 ν = stretch, δ = deformation, a = antisymmetric, s = symmetric.

(a) A liquid phase was present in the 9 cm i.r. cell.

TABLE X

Mass Spectrum of $(\text{CF}_3)_2\text{POSi}(\text{CH}_3)_3$

m/e	I ^a , %	Ion ^b	m/e	I ^a , %	Ion ^b
260	0.08	$\text{C}_5\text{H}_9\text{F}_6\text{POSi}$	125	0.16	$\text{C}_2\text{H}_7\text{FPOSi}$
259	0.22		124	1.58	$\text{C}_2\text{H}_6\text{FPOSi}$
258 ^c	1.97		123	0.79	$\text{C}_2\text{H}_5\text{FPOSi}$
245	0.08	$\text{C}_4\text{H}_6\text{F}_6\text{POSi}$	119	1.44	CF_4P
244	0.22		113	0.93	F_2POSi
243	2.37		109	0.14	CH_3FPOSi
229 ^d	0.06		107	0.14	CHFPOSi
208	0.58	$\text{C}_4\text{H}_9\text{F}_4\text{POSi}$	103	0.13	$\text{C}_2\text{H}_4\text{POSi}$
174	0.17	$\text{C}_3\text{H}_6\text{F}_3\text{POSi}$	100	0.32	CF_3P
149	0.22	$\text{C}_5\text{H}_{15}\text{OSi}_2$	97	1.03	F_2PSi
148	0.47		95	0.14	FPOSi
147	3.00		94	0.71	
145	1.81	$\text{C}_2\text{H}_6\text{F}_2\text{POSi}$	92	0.16	CH_4POSi
144	3.55		91	1.12	
143	13.57		89	$\begin{cases} 0.19 \\ 0.11 \end{cases}$	CH_2POSi
141	0.33	$\text{C}_3\text{H}_9\text{FPOSi}$	85	0.27	F_2PO
140	0.76		83	0.32	C_2PSi
139	9.46		82	0.19	H_3FPSi
131	0.14	$\text{C}_2\text{F}_4\text{P}$	81	3.00	
129	0.25	$\text{CH}_4\text{F}_2\text{POSi}$			
128	0.58	$\text{CH}_3\text{F}_2\text{POSi}$			
127	0.54	$\text{CH}_2\text{F}_2\text{POSi}$			

(continued.....)

TABLE X (continued)

m/e	I ^a , %	Ion ^b	m/e	I ^a , %	Ion
80	0.19	H ₂ POSi	70	0.13	HF ₂ P
79	2.84		69	3.00	CF ₃
78	3.63		67	0.24	HFPO
77	12.78		66	0.32	FPO
76	1.66	HPOSi	65	0.62	CH ₃ FP
75	1.42	C ₃ H ₉ Si	64	0.41	HPO ₂
74	2.37		63	6.47	FOSi
73	6.55		62	0.76	CFP
72	0.73		61	0.54	CH ₅ OSi
71	0.19	C ₃ H ₈ Si	60	0.14	CH ₄ OSi
		C ₃ H ₇ Si	59	1.14	CH ₃ OSi

- (a) Intensities are expressed as percent total ionization, defined as $\sum (\text{Int})_n$ where n refers to all ions with m/e > 58 whose intensity is > 0.4% of the base peak. Left hand brackets enclose reduced intensities of multiplet components at given m/e.
- (b) Ions are listed only once in the Table under the most general designation.
- (c) The identity of this peak was established by mass measurement under high resolution.
- (d) Metastable ion m/e obsd = 229, calcd = 228.6;
 transition $(\text{CF}_3)_2\text{POSi}(\text{CH}_3)_3^+ \rightarrow (\text{CF}_3)_2\text{POSi}(\text{CH}_3)_2^+ + \text{CH}_3$.

TABLE XI

Mass Spectrum of $(\text{CF}_3)_2\text{PSSi}(\text{CH}_3)_3$

m/e	I ^a , %	Ion ^b	m/e	I ^a , %	Ion ^b
370	0.23	C ₄ F ₁₂ P ₂ S	184	0.05	C ₂ H ₅ F ₅ PSi
351	0.08	C ₄ F ₁₁ P ₂ S	183	0.08	
303	0.04	C ₃ F ₉ P ₂ S	182	0.71	
302	0.04		171	0.08	C ₂ HF ₆ P
301	0.73		170	1.20	
290	0.06	C ₅ H ₉ F ₆ POSiS	163	0.43	C ₂ F ₄ PS
284	0.03	C ₅ H ₉ F ₆ PSiS	159	0.16	C ₂ H ₆ F ₂ PSiS
276	0.04		157	0.03	C ₃ H ₉ FPSiS
275	0.08		156	0.04	
274 ^c	0.40		155	0.51	
261	0.08		154	0.04	C ₃ H ₈ FPSiS
260	0.18	C ₄ H ₆ F ₆ PSiS	153	0.04	C ₃ H ₇ FPSiS
259	2.00		152	0.05	C ₃ H ₆ FPSiS
251	0.23	C ₂ F ₇ P ₂ S	151	0.49	CF ₄ PS
229	0.04	C ₂ F ₆ P ₂ S	150	0.59	C ₂ F ₅ P
209	0.06	C ₃ H ₆ F ₄ PSiS	149	1.45	C ₅ H ₁₅ Si ₂ O
205	0.04	C ₄ H ₈ F ₃ PSiS	148	2.83	
204	0.29		147	18.89	
203	0.20	C ₂ HF ₆ PS	145	0.40	C ₂ H ₃ F ₃ PSi
202	6.90		144	0.75	
201	0.11	C ₂ F ₆ PS	143	10.71	
188	0.03	C ₃ H ₄ F ₃ PSiS	(continued.....)		

TABLE XI (continued)

m/e	I ^a , %	Ion ^b	m/e	I ^a , %	Ion ^b
141	0.07	C ₂ H ₅ FPSiS	107	0.04	CH ₄ PSiS
140	0.12		105	0.09	C ₃ H ₉ SiS
139	1.35		103	0.04	C ₃ H ₇ SiS
137	0.12	C ₂ H ₃ FPSiS	102	0.08	C ₃ H ₆ SiS
135	0.18	C ₂ HFPSiS	101	0.81	CHF ₃ P
134	1.30	C ₂ FPSiS	100	1.10	CF ₃ P
133	4.00	CHF ₃ PS	97	0.03	F ₂ PSi
132	0.12	CF ₃ PS	95	0.18	CH ₅ FPSi
131	0.58	C ₂ F ₄ P	94	0.14	CFPS
129	0.08	CHF ₃ PSi	93	0.42	CH ₃ FPSi
128	0.04	CF ₃ PSi	92	0.11	CH ₂ FPSi
127	0.08	C ₂ H ₆ F ₂ PSi	91	{ 0.11 0.27	CHFPSi
125	0.18	C ₂ H ₄ F ₂ PSi	90		C ₂ H ₅ SiS
124	0.04	CH ₂ FPSiS	89	0.04	C ₂ H ₅ SiS
123	0.04	H ₃ F ₃ PS	88	0.09	C ₂ H ₄ SiS
121	0.26	HF ₃ PS	87	0.11	C ₂ H ₃ SiS
120	0.04	CHF ₄ P	85	0.39	C ₂ HSiS
119	0.28	CF ₄ P	84	0.06	C ₂ SiS
117	0.16	HF ₃ PSi	83	4.09	HFPS
116	0.04	C ₂ H ₄ F ₃ P	82	0.90	FPS
115	0.09	C ₂ H ₃ F ₃ P	81	0.74	CF ₂ P
114	0.11	C ₂ H ₂ F ₃ P	79	0.25	HFPSi
113	0.90	CF ₂ PS	(continued.....)		

TABLE XI (continued)

m/e	I ^a , %	Ion ^b	m/e	I ^a , %	Ion ^b
78	{ 0.04 0.40	FPSi	67	0.16	C ₃ H ₃ Si
77	5.10	CH ₅ SiS	67.5	0.27	
76	{ 0.19 0.50	CH ₄ SiS	66	1.90	H ₃ PS
75	{ 0.76 0.24	CPS	65	0.20	H ₂ PS
74	0.45	CH ₃ PSi	64	0.35	HPS
73	{ 6.00 0.11	C ₃ H ₉ Si	63	3.65	CFS
72	0.49	C ₃ H ₈ Si	62	0.27	CFP
71	0.06	C ₃ H ₇ Si	61	0.08	HSiS
70	0.08	C ₃ H ₆ Si	60	0.06	SiS
69	7.49	CF ₃	59	0.61	PSi

-
- (a) Intensities are expressed as percent total ionization, defined as $\sum (\text{Int})_n$ where n refers to all ions with m/e > 58 whose intensity is > 0.2% of the base peak. Left hand brackets enclose reduced intensities of multiplet components at given m/e.
- (b) Ions are listed only once in the Table under the most general designation.
- (c) The identity of this peak was established by mass measurement under high resolution.

(found M, 73; calcd for $\text{CF}_3\text{H:M}$, 70) which was collected at -196° .

(c) (i) With Dimethylamine; Preparation of



A sample of $(\text{CF}_3)_2\text{POSi}(\text{CH}_3)_3$ (0.062 g, 0.24 mmoles) was allowed to react with $(\text{CH}_3)_2\text{NH}$ (0.052 g, 1.15 mmoles) for 5.5 days at room temperature. Vacuum fractionation of the volatile products gave $\text{CF}_3\text{P}[\text{OSi}(\text{CH}_3)_3]\text{N}(\text{CH}_3)_2$ (0.052 g, 0.23 mmoles) containing a trace of $(\text{CH}_3)_3\text{SiN}(\text{CH}_3)_2$, which was collected at both -63° and -84° , $(\text{CH}_3)_2\text{NH}$ (0.040 g, 0.89 mmoles) (found M, 48, calcd for $(\text{CH}_3)_2\text{NH:M}$, 45) which was collected at both -116° and -132° and CF_3H (0.015 g, 0.21 mmoles) (found M, 73; calcd for $\text{CF}_3\text{H:M}$, 70) which was collected at -196° . The white residue remaining in the reaction tube was treated with a large excess of anhydrous HCl at room temperature. Vacuum fractionation of the liberated volatile products gave only $(\text{CF}_3)_2\text{POH}$ (0.001 g, 0.01 mmoles).

(c) (ii) Alkaline Hydrolysis of $\text{CF}_3\text{P}[\text{OSi}(\text{CH}_3)_3]\text{N}(\text{CH}_3)_2$

A sample of $\text{CF}_3\text{P}[\text{OSi}(\text{CH}_3)_3]_2\text{N}(\text{CH}_3)_2$ (0.049 g, 0.21 mmoles) was allowed to react with an excess of degassed NaOH solution for 24 hours at room temperature. Vacuum fractionation of the volatile products gave mixtures (0.018 g) of $[(\text{CH}_3)_3\text{Si}]_2\text{O}$ and $(\text{CH}_3)_2\text{NH}$ in the ratio 1.3:1

(by n.m.r.) collected at both -84° and -116° and CF_3H (0.015 g, 0.21 mmoles) (found M, 68; calcd for CF_3H : M, 70) containing a trace of $(\text{CH}_3)_2\text{NH}$ which was collected at -196° . N.m.r. spectroscopy of the aqueous solution remaining in the reaction tube gave no fluorine signal.

(d) With Anhydrous HCl

A sample of $(\text{CF}_3)_2\text{POSi}(\text{CH}_3)_3$ (0.060 g, 0.23 mmoles) was allowed to react with HCl (0.025 g, 0.69 mmoles) for 27 hours at room temperature. Vacuum fractionation of the volatile products gave $(\text{CF}_3)_2\text{POSi}(\text{CH}_3)_3$ (0.035 g, 0.14 mmoles) which was collected at -63° , a mixture (0.012 g) of $(\text{CF}_3)_2\text{POSi}(\text{CH}_3)_3$ and $(\text{CF}_3)_2\text{POH}$ which was collected at -84° , a mixture (0.020 g) of $(\text{CH}_3)_3\text{SiCl}$ and $(\text{CF}_3)_2\text{PCl}$ which was collected at -116° and HCl (0.021 g, 0.58 mmoles) which was collected at -196° . The above mixtures were resealed in a clean reaction tube and the reaction was allowed to proceed for a further 5.5 days at room temperature. Vacuum fractionation of the volatile products resulting after further reaction gave $(\text{CF}_3)_2\text{POSi}(\text{CH}_3)_3$ (0.029 g, 0.11 mmoles) which was collected at -63° , a mixture (0.021 g) of $(\text{CF}_3)_2\text{POSi}(\text{CH}_3)_3$ with traces of $[(\text{CH}_3)_3\text{Si}]_2\text{O}$ and $(\text{CF}_3)_2\text{POH}$ which was collected at -84° , a mixture (0.022 g) of $(\text{CH}_3)_3\text{SiCl}$, $(\text{CF}_3)_2\text{PCl}$ and trace of an unidentified compound which was collected at -116° , a mixture (0.007 g) of $(\text{CH}_3)_3\text{SiCl}$ and $(\text{CF}_3)_2\text{PCl}$ which was

collected at -132° and HCl (0.018 g, 0.50 mmoles) (found M, 37, calcd for HCl M, 36) which was collected at -196° . N.m.r. spectroscopy of the -63° and -84° mixtures indicated the presence of $(\text{CF}_3)_2\text{POSi}(\text{CH}_3)_3$, $(\text{CF}_3)_2\text{POH}$ and $[(\text{CH}_3)_3\text{Si}]_2\text{O}$ in the ratio 13.5:1.1:1.

(e) Pyrolysis

A sample of $(\text{CF}_3)_2\text{POSi}(\text{CH}_3)_3$ (0.046 g, 0.18 mmoles) heated in a sealed tube for 6 days at 195° was quantitatively recovered (0.047 g, 0.18 mmoles). N.m.r. spectroscopy (^{19}F and ^1H) of the recovered sample showed the presence of only $(\text{CF}_3)_2\text{POSi}(\text{CH}_3)_3$.

5. Reactions of $(\text{CF}_3)_2\text{PSSi}(\text{CH}_3)_3$

(a) With Water

A sample of $(\text{CF}_3)_2\text{PSSi}(\text{CH}_3)_3$ (0.075 g, 0.27 mmoles) was combined with an excess of degassed distilled H_2O and allowed to react for 6 days at room temperature. Vacuum fractionation of the volatile products gave $[(\text{CH}_3)_3\text{Si}]_2\text{O}$ (0.024 g, 0.15 mmoles) which was collected at -84° , $(\text{CH}_3)_3\text{SiF}$ (0.002g, 0.02 mmoles) which was collected at -132° , and a mixture (0.032 g) (found M, 56.8) of H_2S and CF_3H which was collected at -196° .

The quantities of CF_3H and H_2S were determined by reacting the mixture of the gases with aqueous lead acetate solution whereupon H_2S precipitated as lead sulfide

leaving CF_3H as the volatile products. Recovery of CF_3H in vacuum gave (0.019 g, 0.27 mmoles) with the purity confirmed by the molecular weight (found M, 68; calcd for CF_3H :M, 70) and the infrared spectrum of the fraction.

Neutralization of the aqueous solution remaining in the reaction tube with NaOH gave a solution containing the $\text{CF}_3\text{P}(\text{H})\text{O}_2^-$ ion according to the n.m.r. spectrum.²⁰ A mass spectrum of this salt gave an ion at 134 identified as $\text{CF}_3\text{PO}_2\text{H}_2$ by accurate mass measurement (found m/e 133.9736; calcd for $\text{CH}_2\text{F}_3\text{O}_2\text{P}$, 133.9744).

(b) Alkaline Hydrolysis

A sample of $(\text{CF}_3)_2\text{PSSi}(\text{CH}_3)_3$ (0.102 g, 0.37 mmoles) was allowed to react with a 10% NaOH solution for several days at room temperature. The volatile products were $[(\text{CH}_3)_3\text{Si}]_2\text{O}$ (0.029 g, 0.18 mmoles) which was collected at -84° , and CF_3H (0.049 g, 0.70 mmoles) (found M, 73; calcd for CF_3H :M, 70) which was collected at -196° .

On addition of a solution of lead acetate to the remaining NaOH solution in the reaction tube, a white precipitate was formed presumably due to precipitation of $\text{HPO}_3^{=}$ by Pb^{++} ions. With further addition of lead acetate solution, a black precipitate was formed indicating the presence of $\text{S}^{=}$ in the solution.

(c) With Dimethylamine

$(\text{CF}_3)_2\text{PSSi}(\text{CH}_3)_3$ (0.067 g, 0.24 mmoles) and $(\text{CH}_3)_2\text{NH}$ (0.039 g, 0.87 mmoles) were allowed to react for 7 days at room temperature. The resultant mixture of products was a pale yellowish colored liquid. The volatile products obtained included an unidentified compound (0.002 g) which was collected at -63° , $(\text{CH}_3)_3\text{SiN}(\text{CH}_3)_2$ (0.028 g, 0.24 mmoles) which was collected at -84° and unreacted $(\text{CH}_3)_2\text{NH}$ (0.017 g, 0.38 mmoles) which was collected at -116° . The white residue remaining in the reaction tube was treated with an excess of anhydrous HCl whereupon a quantity of $(\text{CF}_3)_2\text{PSH}$ (0.044 g, 0.22 mmoles) (found M, 208; calcd for $(\text{CF}_3)_2\text{PSH:M}$, 202) was obtained along with unreacted HCl.

(d) With Anhydrous HCl

A sample of $(\text{CF}_3)_2\text{PSSi}(\text{CH}_3)_3$ (0.059 g, 0.22 mmoles) was allowed to react with anhydrous HCl (0.013 g, 0.36 mmoles) for 8 days at room temperature. Vacuum fractionation of the products gave a mixture (0.001 g) of $(\text{CF}_3)_2\text{PSSi}(\text{CH}_3)_3$ and $[(\text{CF}_3)_2\text{P}]_2\text{S}$ which was collected at -63° , an unseparated mixture (0.065 g) of $(\text{CH}_3)_3\text{SiCl}$ and $(\text{CF}_3)_2\text{PSH}$ in 1:1.2 ratio (by n.m.r.) which was collected at both -84° and -116° and unreacted HCl (0.004 g, 0.11 mmoles) which was collected at -196° .

(e) Pyrolysis

A sample of $(\text{CF}_3)_2\text{PSSi}(\text{CH}_3)_3$ (0.080 g, 0.29 mmoles) was heated to 195° for 9 days. Vacuum condensation of the products gave mixtures (tot. wt. 0.068 g) of $(\text{CF}_3)_2\text{PSSi}(\text{CH}_3)_3$, $[(\text{CF}_3)_2\text{P}]_2\text{S}$ and several unidentified compounds which were collected at both -63° and -84° , a mixture (0.006 g) of $(\text{CH}_3)_3\text{SiF}$ and an unidentified compound which was collected at -116° and a trace of an unidentified compound which was collected at -196° . The glass wall of the reaction tube after removal of the volatile products had been rendered opaque. Analysis of the combined -63° and -84° mixtures by ^{19}F and ^1H n.m.r. indicated the presence of a variety of compounds with the chemical shifts (ϕ, τ) and coupling constants (J) shown in the list. Identities of the compounds are also indicated in the list where clear assignments can be made.

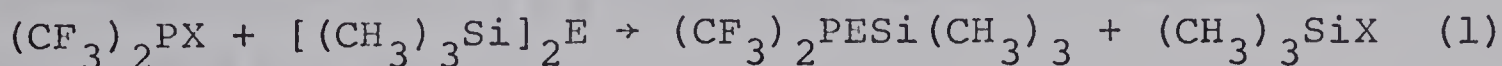
^1H		^{19}F				<u>Identity</u>
τ	h^b (cm)	ϕ	J (cps)	h^b (cm)	App ^a	
9.40 ^c	9.1	58.7	79	1.6	d	$(\text{CF}_3)_2\text{PSSi}(\text{CH}_3)_3$
9.51	0.1	-	-	-	-	?
9.67	0.1	-	-	-	-	$[(\text{CH}_3)_3\text{Si}]_2\text{S}$
9.86	0.7	-	-	-	-	$[(\text{CH}_3)_3\text{Si}]_2$
-	-	56.4	83	0.2	d	$[(\text{CF}_3)_2\text{P}]_2\text{S}$
		58.9	79	0.2	d	?

(a) Appearance of spectrum due to spin-spin splitting pattern.

- (b) Total integrated intensity of spin splitting pattern
 - (c) Doublet with $J = 1.5$ cps
 - (d) Doublet
-

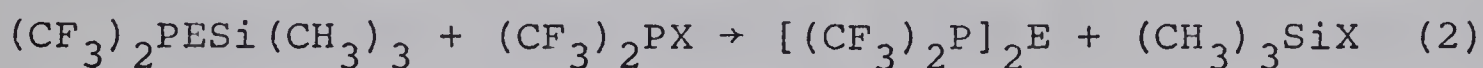
6. Results and Discussion

The reaction of phosphorus-halides with the oxy and thio bridged disilanes $[(CH_3)_3Si]_2E$ ($E = O, S$) is a convenient method of preparing compounds containing the P-E-Si bridge system. This method had previously been reported³⁷ to provide a nearly quantitative yield of $(CF_3)_2POSi(CH_3)_3$ as a result of heating $[(CH_3)_3Si]_2O$ with $(CF_3)_2PCl$ at 100° for five days. However when this reaction was repeated by the author under the same conditions, only trace amounts of $(CH_3)_3SiCl$ and $(CF_3)_2POSi(CH_3)_3$ were obtained in contrast to the nearly quantitative yield (eqn (1) reported elsewhere.³⁷ Similar results were obtained at reaction temperature of 160° . We have found that the compound $(CF_3)_2POSi(CH_3)_3$ is best prepared from the almost quantitative reaction of $(CF_3)_2PF$ with $[(CH_3)_3Si]_2O$ at 100° for several days according to eqn (1) ($E = O, X = F$).

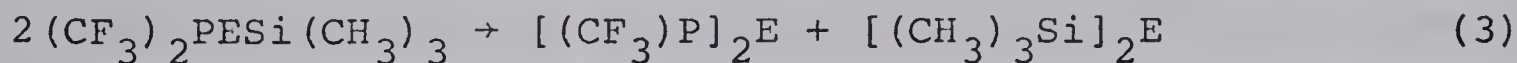


However, even in this case, a trace of $[(CF_3)_2P]_2O$ was found among the products indicating that a side reaction

had taken place possibly according to eqn (2) ($E = O$, $X = F$). The $[(CF_3)_2P]_2O$ product does not likely come from the thermal decomposition of the initially formed $(CF_3)_2POSi(CH_3)_3$ product (e.g. eqn (3), $E = O$) since $(CF_3)_2POSi(CH_3)_3$ has been found to be stable to decomposition up to 195° . Hence the process described by equation (2) is the most reasonable alternative route to formation of $[(CF_3)_2P]_2O$.



Similarly, $(CF_3)_2PSSi(CH_3)_3$ was prepared almost quantitatively according to reaction (1) ($E = S$, $X = Cl$) along with a small amount of $[(CF_3)_2P]_2S$. In this case the $[(CF_3)_2P]_2S$ product could have been obtained from the condensation reaction (2), $E = S$



or from the pyrolysis of $(CF_3)_2PSSi(CH_3)_3$. A separate experiment indicated that heating to 195° resulted in the loss of 10% of the original $(CF_3)_2PSSi(CH_3)_3$ with the formation of $[(CF_3)_2P]_2S$. The presence of the variety of other unidentified products suggests that the thermal decomposition of $(CF_3)_2PSSi(CH_3)_3$ is more complex than is suggested by eqn (3).

Nuclear magnetic resonance parameters of both the phosphino oxy-silane and thio-silane are given in Table XIV (Appendix). We find that the chemical shifts and

coupling constants are similar and compatible with trivalent bis(trifluoromethyl)phosphorus compounds however the ^1H chemical shift reported elsewhere ³⁷ for $(\text{CF}_3)_2\text{POSi}(\text{CH}_3)_3$ appears to be in error since it is not in agreement with the present result nor is their value compatible with all of the $\text{Si}(\text{CH}_3)_3$ τ values found in this study.

Of interest is the behavior of the ^1H n.m.r. spectrum of $\text{CF}_3\text{P}[\text{OSi}(\text{CH}_3)_3]\text{N}(\text{CH}_3)_2$ with ^{31}P decoupling irradiation as shown in Figure 5. The protons in the $\text{OSi}(\text{CH}_3)_3$ substituent which appeared as a 0.3 cycle doublet in the ^1H n.m.r. spectrum collapsed upon irradiation with the ^{31}P resonant frequency into a singlet indicating that this doublet arises from coupling of the protons in the $\text{OSi}(\text{CH}_3)_3$ substituent with the phosphorus atom. The ^1H n.m.r. spectrum of the $\text{N}(\text{CH}_3)_2$ substituent consists of a doublet of quartets due to the coupling of the protons with the phosphorus and fluorine nuclei. The doublet of quartets collapsed on ^{31}P irradiation into a simple quartet confirming that the major doublet observed in the original spectrum is due to the coupling of the phosphorus nuclear spin of 1/2 with the equivalent protons in the $\text{N}(\text{CH}_3)_2$ group.

The chemical behavior of the $(\text{CF}_3)_2\text{PESi}(\text{CH}_3)_3$ ($\text{E} = \text{O}, \text{S}$) compound agrees with a formulation involving a tervalent phosphorus and a P-E-Si bridge bond. The reaction of either of the compounds with water gave one mole of

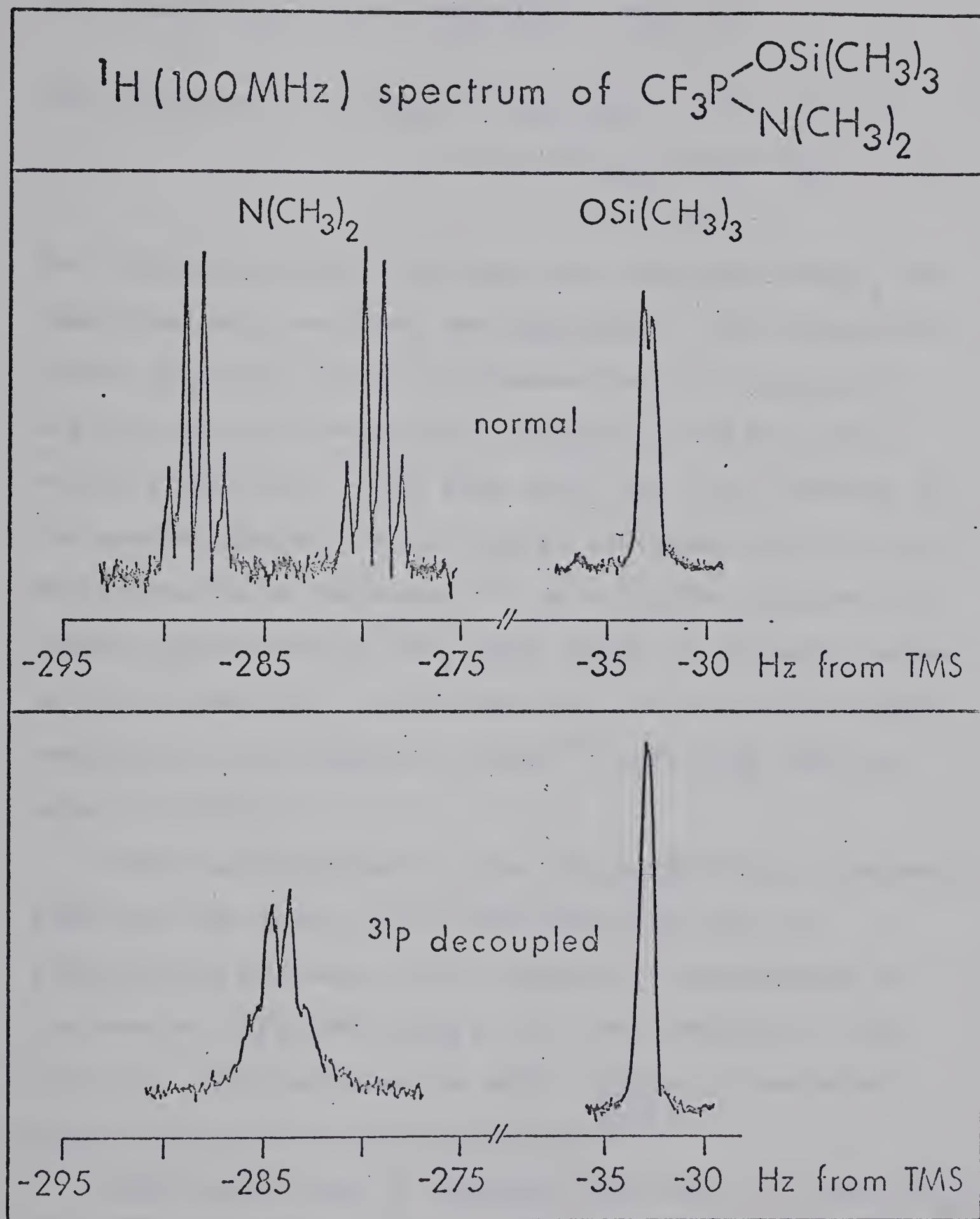
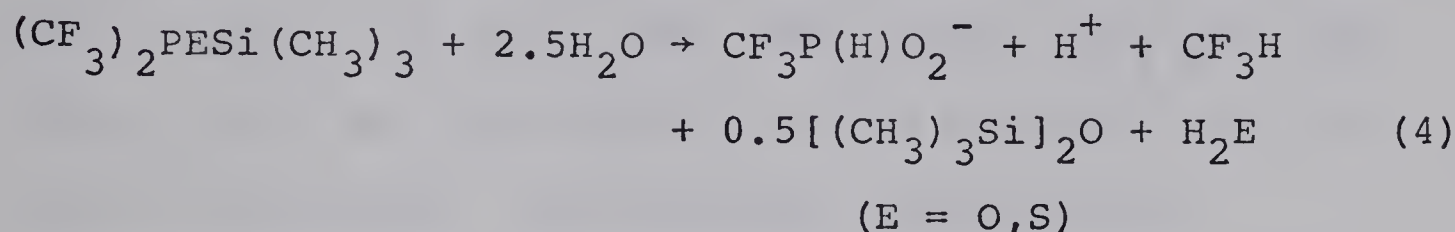


FIGURE 5. The ^1H n.m.r. spectrum of $\text{CF}_3\text{P}[\text{OSi}(\text{CH}_3)_3]\text{N}(\text{CH}_3)_2$ with ^{31}P decoupling.

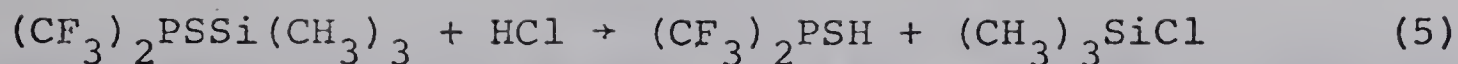
CF_3H and one-half mole of $[(\text{CH}_3)_3\text{Si}]_2\text{O}$ for every mole of $(\text{CF}_3)_2\text{PSi}(\text{CH}_3)_3$ taken according to eqn (4).



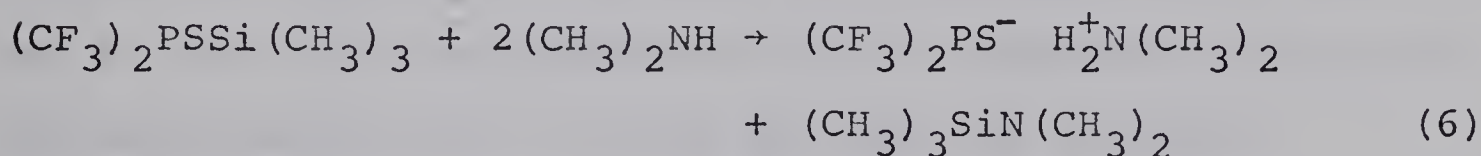
The hydrogen sulfide liberated from $(\text{CF}_3)_2\text{PSSi}(\text{CH}_3)_3$ was quantitatively recovered and identified. The formation of the $\text{CF}_3\text{P}(\text{H})\text{O}_2^-$ ion²⁰ indicated that the compounds are derivatives of tervalent phosphorus and not pentavalent phosphorus. This same anion has been observed in the neutral hydrolysis of several tervalent bistrifluoromethylphosphorus compounds.²⁰ In a similar fashion the neutral hydrolysis of $(\text{CF}_3)_2\text{PSH}$, which is probably formed as an intermediate in the hydrolysis of the P-SSi bridge compound has been shown to yield²⁰ H_2S , CF_3H and the anion $\text{CF}_3\text{P}(\text{H})\text{O}_2^-$.

Alkaline hydrolysis of the $(\text{CF}_3)_2\text{PSi}(\text{CH}_3)_3$ compounds liberated two moles of CF_3H and one-half mole of $[(\text{CH}_3)_3\text{Si}]_2\text{O}$ per mole of the compound. Furthermore in the case of $(\text{CF}_3)_2\text{PSSi}(\text{CH}_3)_3$, S^- ions remained in the solution. This behavior is again typical of tervalent rather than pentavalent phosphorus.^{29,34}

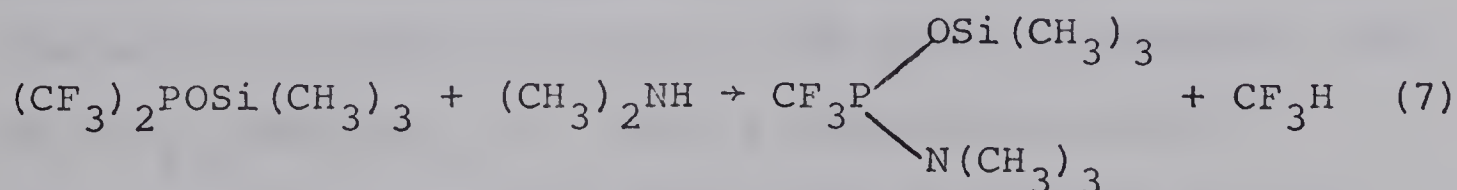
Molar quantities of anhydrous HCl and $(\text{CF}_3)_2\text{PSSi}(\text{CH}_3)_3$ reacted to give $(\text{CF}_3)_2\text{PSH}$ and $(\text{CH}_3)_3\text{SiCl}$ in nearly quantitative yields according to eqn (5).



In contrast, the reaction of $(\text{CF}_3)_2\text{POSi}(\text{CH}_3)_3$ with HCl gave a mixture of $(\text{CF}_3)_2\text{POH}$, $(\text{CH}_3)_3\text{SiCl}$, $(\text{CF}_3)_2\text{PCl}$ and $[(\text{CH}_3)_3\text{Si}]_2\text{O}$ but the majority of the compound was recovered unchanged. Dimethylamine reacted with $(\text{CF}_3)_2\text{PSSi}(\text{CH}_3)_3$ to give a nearly quantitative yield of $(\text{CH}_3)_3\text{SiN}(\text{CH}_3)_2$ and a white salt formulated as the dimethylamine adduct⁴⁰ of $(\text{CF}_3)_2\text{PSH}$ eqn (6).



Reaction of this white salt with anhydrous HCl gave an almost quantitative yield of $(\text{CF}_3)_2\text{PSH}$ ⁴⁰ to complete the mass balance represented by eq (6). Thus the white salt is properly formulated as the adduct $(\text{CF}_3)_2\text{PS}^- \text{H}_2\text{N}^+(\text{CH}_3)_2$ which has been synthesised elsewhere.⁴⁰ In contrast the reaction of $(\text{CF}_3)_2\text{POSi}(\text{CH}_3)_3$ with $(\text{CH}_3)_2\text{NH}$ gave CF_3H in 88% yield and a new compound containing a P-N $(\text{CH}_3)_2$ as well as a P-OSi $(\text{CH}_3)_3$ substituent. The majority of the reaction proceeded according to eqn (7).



A small amount of white solid remained in the reaction tube

which was identified as the $(\text{CF}_3)_2\text{PO}^- + \text{H}_2\text{N}(\text{CH}_3)_2$ adduct by the reaction with HCl to give $(\text{CF}_3)_2\text{POH}$.⁴¹ Thus it was possible to account for the apparent loss of 12% of the $(\text{CF}_3)_2\text{P}$ groups in the reaction. The new amino oxysilane $\text{CF}_3\text{P}[\text{OSi}(\text{CH}_3)_3]\text{N}(\text{CH}_3)_2$ was identified by mass spectroscopy (Table XII) including accurate mass measurement of the parent ion (calcd for $\text{CF}_3\text{P}[\text{O}^{28}\text{Si}(\text{CH}_3)_3]\text{N}(\text{CH}_3)_3$, m/e 233.0613; found: m/e 233.0610), by the n.m.r. spectrum (Table XIV, Appendix), by the i.r. spectrum (Table XIII), and by the alkaline hydrolysis of the compound which gave one molar equivalent of CF_3H per mole of compound.

The cleavage of the S-Si bond in $(\text{CF}_3)_2\text{PSSi}(\text{CH}_3)_3$ by dimethylamine yields the expected products $(\text{CF}_3)_2\text{PSH}$ (as its dimethylamine adduct) and the aminosilane. The most likely pathway probably involves attack at Si by the base followed by proton transfer and separation of the Si-N compound. On the other hand, the electron withdrawing effects of both CF_3 and $\text{OSi}(\text{CH}_3)_3$ groups is to make the phosphorus atom in $(\text{CF}_3)_2\text{POSi}(\text{CH}_3)_3$ the most acidic in molecule rather than the silicon atom and it therefore seems reasonable to suggest that the reaction proceeds through the attack of base on the acidic phosphorus atom of $(\text{CF}_3)_2\text{POSi}(\text{CH}_3)_3$ to form a tetracoordinated phosphorus intermediate which then decomposes to give CF_3H and the new compound according to eqn (8).

TABLE XII

Mass Spectrum of $\text{CF}_3\text{P}[\text{OSi}(\text{CH}_3)_3]\text{N}(\text{CH}_3)_2$

m/e	$I^a, \%$	Ion b	m/e	$I^a, \%$	Ion b
233 ^c	0.12	$\text{C}_6\text{H}_{15}\text{F}_3\text{NPOSi}$	144	0.37	$\text{C}_2\text{H}_7\text{F}_2\text{POSi}$
232	0.17	$\text{C}_6\text{H}_{14}\text{F}_3\text{NPOSi}$	143	0.57	$\text{C}_2\text{H}_6\text{F}_2\text{POSi}$
213	0.17	$\text{C}_6\text{H}_4\text{F}_2\text{NPOSi}$	139	0.54	$\text{C}_3\text{H}_9\text{FPOSi}$
205	0.10	$\text{C}_4\text{H}_{11}\text{F}_3\text{NPOSi}$	131	0.20	$\text{C}_2\text{F}_4\text{P}$
182	0.15	$\text{C}_5\text{H}_{14}\text{FNPOSi}$	125	0.42	CF_2POSi
180	0.12	$\text{C}_5\text{H}_{10}\text{FNPOSi}$	124	0.17	CHFNPOSi
179	0.81		123	0.25	
178	5.17		122	0.39	
177	0.25	$\text{C}_5\text{H}_9\text{FNPOSi}$	121	4.18	
176	0.59	$\text{C}_5\text{H}_8\text{FNPOSi}$	120	0.25	CFNPOSi
170	0.17	$\text{C}_4\text{H}_{12}\text{FNPOSi}$	107	0.22	CHFPOSi
169	0.42		103	0.20	CH_2NPOSi
168	4.22		102	1.60	CHNPOSi
166	1.13	$\text{C}_5\text{H}_{15}\text{NPOSi}$	94	1.01	FPOSi
165	3.03		92	0.54	H_3NPOSi
164	29.53		91	0.37	H_2NPOSi
163	0.22	$\text{C}_5\text{H}_{14}\text{NPOSi}$	90	0.42	HNPOSi
152	0.20	$\text{C}_3\text{H}_3\text{F}_2\text{POSi}$	89.5	0.15	
151	0.25	$\text{C}_3\text{H}_2\text{F}_2\text{POSi}$	89	0.89	NPOSi
150	0.17	$\text{C}_5\text{H}_{15}\text{OSi}_2$	88	0.62	CHPOSi
149	0.59		82	0.20	CHF_2P
148	1.16				
147	7.39				

(continued.....)

TABLE XII (continued)

<u>m/e</u>	<u>I^a, %</u>	<u>Ion^b</u>	<u>m/e</u>	<u>I^a, %</u>	<u>Ion</u>
79	0.47	H ₂ POSi	72	0.22	C ₃ H ₈ Si
78	0.52		69	0.20	CF ₃
77	4.18		66	0.94	FPO
76	0.74	HPOSi	63	0.64	FOSi
75	1.53	POSi	62	0.15	HPON
74.5	1.13	C ₃ H ₉ Si	61	0.39	PON
74	1.36		60	1.08	CH ₄ OSi
73	14.78		59	1.40	CH ₃ OSi

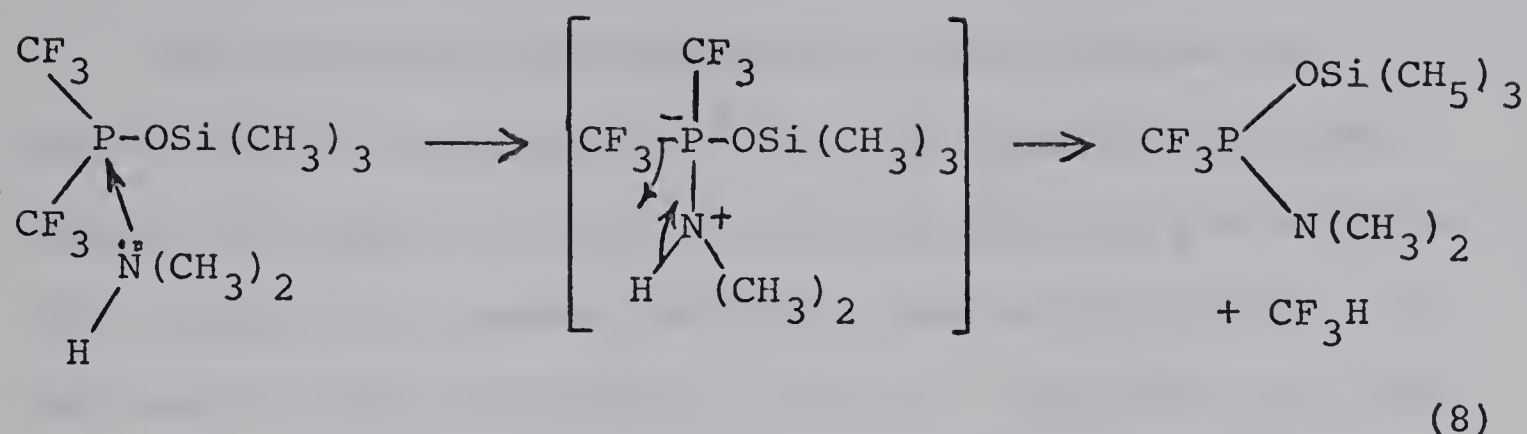
- (a) Intensities are expressed as percent total ionization; defined as $\sum (\text{Int})_n$ where n refers to all ions with $m/e > 58$ whose intensity is 0.4% of the base peak. Left hand brackets enclose reduced intensities of multiplet components at given m/e .
- (b) Ions are listed only once in the Table under the most general designation.
- (c) The identity of this peak was established by mass measurement under high resolution.

TABLE XIII

Infrared Spectrum of $\text{CF}_3\text{P}[\text{OSi}(\text{CH}_3)_3]\text{N}(\text{CH}_3)_2$

3010	vw		1122	vs	$\nu(\text{C-F})$
2968	m	$\nu(\text{C-H})$	1066	w	
2935	w	$\nu(\text{C-H})$	1027	m	$\nu(\text{Si-O})$
2903	m	$\nu(\text{C-H})$	990	s	$\delta[\text{N}-(\text{CH}_3)_2]$
2855	w	$\nu(\text{C-H})$	958	vs	$\nu(\text{P-O})$
2813	w	$\nu(\text{C-H})$	855	vs	$\nu(\text{Si-C})$
1573	vw		759	m	$\delta(\text{CF}_3)$
1485	vw		688	m	
1462	w		666	vw	
1414	vw		606	w	
1294	m	$\delta(\text{N-CH}_3)$	538	w	
1265	s	$\delta(\text{Si-CH}_3)$	470	w	$\nu_a(\text{P-CF}_3)$
1190	vs	$\nu(\text{C-F})$	420	w	

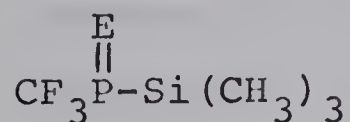
s = strong, m = medium, w = weak, v = very, sh = shoulder
 ν = stretch, δ = deformation, a = antisymmetric, s = symmetric.



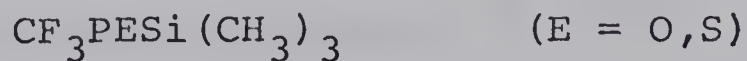
The difference in the reaction pathway and products between P-O-Si and P-S-Si systems reflects a shift in the relative acidities of P and Si and may be in part due to a very strong bonding situation in the P-O-Si bridge due to extensive π bonding between the oxygen and both silicon and phosphorus. Certainly whatever the reasons it is clear that the P-O-Si bridge is not readily cleaved by either the acidic or the basic protic reagents used in this study in marked contrast to the ready cleavage of the analogous P-S-Si bridge by these reagents.

7. Structures of the Phosphino Silanes

There are two possible isomeric structures that can reasonably be suggested for $(\text{CF}_3)_2\text{PESi}(\text{CH}_3)_3$ ($\text{E} = \text{O}, \text{S}$). One structure has a pentavalent phosphorus with a P-E double bond (I) and the other has a tervalent phosphorus with a P-E-Si bridge bond (II).



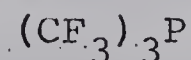
I



II

The tervalent phosphorus(II) could follow an Arbuzov-like rearrangement⁴² to the pentavalent form. However the spectra indicate clearly that only structure (II) occurs in agreement with the chemical behavior. In the case of $(\text{CF}_3)_2\text{POSi}(\text{CH}_3)_3$, the i.r. spectrum, in good agreement with that of Burg and Basi,³⁷ showed no strong bands in 1280 cm^{-1} to 1500 cm^{-1} region which contains the P=O stretching frequency. For example, the P=O stretching bands are found at 1349 cm^{-1} in $(\text{CF}_3)_3\text{P=O}$ ¹⁷ and 1332 cm^{-1} in $(\text{CF}_3)_2\text{P(O)Cl}$.¹⁷ Furthermore a strong band at 1052 cm^{-1} can be assigned to Si-O stretching in agreement with methylpolysiloxanes³³ which have bands at 1052 cm^{-1} . In the case of $(\text{CF}_3)_2\text{PSSi}(\text{CH}_3)_3$, no strong i.r. bands were found in the 700 to 800 cm^{-1} region which could be assigned to P=S stretching.³⁴ The weak band at 527 cm^{-1} could be assigned to P-S stretching which is in agreement with the bands observed in $\text{CH}_3\text{SP}(\text{CF}_3)_2$ and $t\text{-C}_4\text{H}_9\text{SP}(\text{CF}_3)_2$ (523 cm^{-1} and 530 cm^{-1} respectively).⁴³ Finally the ^{19}F n.m.r. spectra of $(\text{CF}_3)_2\text{PESi}(\text{CH}_3)_3$ (E = O, S) (Table XIV, Appendix) shows characteristic doublets with chemical shifts and coupling constants which can be reasonably associated with P-F coupling between the CF_3 and a tervalent, tricoordinate phosphorus atom rather than pentavalent phosphorus.^{31,32,40} The ^{31}P n.m.r. spectra of $(\text{CF}_3)_2\text{PESi}(\text{CH}_3)_3$ (E = O, S) show in

each case a seven line pattern (Table XIV, Appendix) with an intensity distribution in good agreement with that expected for the septet pattern arising from six equivalent fluorine atoms to further confirm the presence of two CF_3 groups on phosphorus atom.

CHAPTER VISome Reactions of Tris(trifluoromethyl)phosphine

The literature contains few reports of the reactions of $(\text{CF}_3)_3\text{P}$. It has been found to react smoothly with Cl_2 at -40° to give $(\text{CF}_3)_3\text{PCl}_2$ ⁹, with NO_2 to give $(\text{CF}_3)_3\text{P=O}$ ¹⁷, with SF_4 at 25° to give $(\text{CF}_3)_3\text{PF}_2$ ⁴⁴ and with CH_3I at 240° to give $(\text{CF}_3)_2\text{PCH}_3$ ⁴⁴ all in very good yields (>90%). Furthermore it has been reported that $(\text{CF}_3)_3\text{P}$ reacted readily with liquid NH_3 at about -70° to give $(\text{CF}_3)_2\text{PNH}_2$, CF_3H and an unidentified material of low volatility.⁴⁵ $(\text{CF}_3)_3\text{P}$ will only react with I_2 at a temperature greater than 100° ,⁹ and with S at 200° to give $(\text{CF}_3)_3\text{P=S}$.²⁹ On the other hand $(\text{CF}_3)_3\text{P}$ was also reported not to react with H_2O even at 100° ⁴⁶ nor with S or CS_2 up to 200° .⁹

This Chapter is concerned with some further reactions of $(\text{CF}_3)_3\text{P}$ with acids, bases and alcohols.

1. Reactions of Tris(trifluoromethyl)phosphine(a) With Dimethylamine

$(\text{CF}_3)_3\text{P}$ (0.255 g, 0.95 mmol) and $(\text{CH}_3)_2\text{NH}$ (0.049 g, 1.09 mmol) were allowed to react for 6 hours at room temperature. The volatile products were $(\text{CF}_3)_2\text{PN}(\text{CH}_3)_2$ (0.020 g, 0.09 mmol, 10%) which was collected at -84° ,

a mixture (0.233 g) of $(\text{CH}_3)_2\text{NH}$ and $(\text{CF}_3)_3\text{P}$ which was collected at -116° and CF_3H (0.009 g, 0.13 mmoles) which was collected at -196° . A yellowish residue presumably $[(\text{CH}_3)_2\text{NH}_2^+ \text{I}^-]$ remained in the reaction tube.

In another experiment a sample of $(\text{CF}_3)_3\text{P}$ (0.435 g, 1.83 mmoles) was combined with $(\text{CH}_3)_2\text{NH}$ (0.094 g, 2.09 mmoles). Upon warming to room temperature a reaction occurred forming a trace of a white solid and a volatile yellowish liquid. The former was probably due to a trace of $(\text{CF}_3)_2\text{PI}$ impurity in the $(\text{CF}_3)_3\text{P}$. Vacuum fractionation of the volatile products gave $(\text{CF}_3)_2\text{PN}(\text{CH}_3)_2$ (0.267 g, 1.25 mmoles, 68%) which was collected at -84° , a mixture (0.149 g) of $(\text{CF}_3)_3\text{P}$ and $(\text{CH}_3)_2\text{NH}$ which was collected at -116° and CF_3H (0.093 g, 1.33 mmoles) which was collected at -196° . A trace of white solid and a trace of nonvolatile yellowish liquid remained in the reaction tube.

In a third experiment, $(\text{CF}_3)_3\text{P}$ (0.233 g, 0.98 mmoles) was treated with a small amount of $(\text{CH}_3)_2\text{NH}$ to remove any $(\text{CF}_3)_2\text{PI}$ present as impurity and subsequently allowed to react with $(\text{CH}_3)_2\text{NH}$ (0.051 g, 1.14 mmoles) for seven days at room temperature. Vacuum fractionation gave $(\text{CF}_3)_2\text{PN}(\text{CH}_3)_2$ (0.133 g, 0.53 mmoles, 54%) which was collected at -84° , a mixture (0.084 g) of $(\text{CF}_3)_3\text{P}$ and

$(\text{CH}_3)_2\text{NH}$ which was collected at -116° and CF_3H (0.039 g, 0.56 mmol) (found M, 73; calcd for CF_3H M, 70) which was collected at -196° . No residue remained in the reaction tube.

(b) With Methylamine

A sample of $(\text{CF}_3)_3\text{P}$ (0.263 g, 1.11 mmol) was allowed to react with CH_3NH_2 (0.032 g, 1.03 mmol) for ten hours at 100° . Vacuum fractionation of the volatile products gave $(\text{CF}_3)_2\text{PN}(\text{H})\text{CH}_3$ (0.109 g, 0.55 mmol) which was collected at -84° and CF_3H (0.044 g, 0.63 mmol, 57%) (found M, 71; calcd for CF_3H M, 70) which was collected at -196° . A white and yellow residue remained in the reaction tube. The rest of the volatile products were neither weighed nor analysed by i.r. spectroscopy.

In another experiment, $(\text{CF}_3)_3\text{P}$ (0.478 g, 2.01 mmol) and CH_3NH_2 (0.067 g, 2.16 mmol) were allowed to react for three days at room temperature. After one hour at room temperature, white solids were formed and the solution was pale yellow. Vacuum fractionation of the volatile products gave $(\text{CF}_3)_2\text{PN}(\text{H})\text{CH}_3$ (0.288 g, 1.45 mmol, 72%) which was collected at -116° and CF_3H (0.101 g, 1.44 mmol) (found M, 73; calcd for CF_3H :M, 70) which was collected at -196° .

(c) With Ammonia

$(\text{CF}_3)_3\text{P}$ (0.260 g, 1.09 mmol) was treated with a

small amount of $(\text{CH}_3)_2\text{NH}$ to remove any $(\text{CF}_3)_2\text{PI}$ impurity and subsequently allowed to react with NH_3 (0.018 g, 1.06 mmoles) for two days at 100° . The volatile products were the $[(\text{CF}_3)_2\text{P}]_2\text{NH-NH}_3$ adduct (0.008 g, 0.002 mmoles) which was collected at -63° , a mixture (0.041 g) of $(\text{CF}_3)_2\text{PNH}_2$ and NH_3 which was collected at -84° , a mixture (0.207 g) of unreacted $(\text{CF}_3)_3\text{P}$ and NH_3 which was collected at -116° and CF_3H (0.019 g, 0.27 mmoles) which was collected at -196° . No residue remained in the reaction tube.

In another reaction a sample of $(\text{CF}_3)_3\text{P}$ (0.211 g, 0.89 mmoles) was allowed to react with NH_3 (0.014 g, 0.82 mmoles) for 20 days at room temperature. Vacuum fractionation of the volatile products gave the $[(\text{CF}_3)_2\text{P}]_2\text{NH-NH}_3$ adduct (0.024 g, 0.06 mmoles) which was collected at -63° , a mixture (0.042 g) of $(\text{CF}_3)_2\text{PNH}_2$ and NH_3 which was collected at -84° , mixtures (0.163 g) of $(\text{CF}_3)_3\text{P}$ and NH_3 which were collected at both -116° and -132° and a mixture of CF_3H and NH_3 which was collected at -196° . No residue remained in the reaction tube.

The quantities of CF_3H and NH_3 in the -196° trap were determined by reacting the mixture first with HCl to give NH_4^+Cl^- salt and then with $(\text{CH}_3)_3\text{N}$ to remove the excess HCl .

Vacuum fractionation of the volatile products gave CF_3H (0.028 g, 0.40 mmoles). The quantities of $(\text{CF}_3)_3\text{P}$ and NH_3 in the -116° and -132° traps were also determined by reacting the mixture with HCl . Vacuum fractionation gave $(\text{CF}_3)_3\text{P}$ (0.127 g, 0.53 mmoles).

(d) With Anhydrous HBr.

$(\text{CF}_3)_3\text{P}$ (0.531 g, 2.15 mmoles) and HBr (0.191 g, 2.36 mmoles) did not react at room temperature for 6 days nor at 100° for 5 days. However, at 160° for 4 days, vacuum fractionation of the volatile products gave $(\text{CF}_3)_2\text{PBr}$ (0.015 g, 0.06 mmoles) which was collected at -96° (identified by n.m.r.), $(\text{CF}_3)_3\text{P}$ (0.497 g, 2.09 mmoles) (found M, 239; calcd for $(\text{CF}_3)_3\text{P}$; M, 238) which was collected at -116° and a mixture (0.187 g) of HBr and CF_3H which was collected at -196° .

In a second experiment, $(\text{CF}_3)_3\text{P}$ (0.460 g, 1.93 mmoles) and HBr (0.178 g, 2.20 mmoles) were allowed to react at 185° for 20 days. The volatile products were a mixture (0.134 g) of $(\text{CF}_3)_2\text{PBr}$ and CF_3PBr_2 which was collected at both -84° and -96° and identified by n.m.r. and mass spectroscopy, a mixture (0.303 g) of $(\text{CF}_3)_3\text{P}$ and a trace of $(\text{CF}_3)_2\text{PBr}$ which was collected at -116° and a mixture of CF_3H and HBr which was collected at -196° .

(e) With Anhydrous HCl

$(\text{CF}_3)_3\text{P}$ (0.446 g, 1.87 mmoles) and HCl (0.072 g, 2.00 mmoles) did not react for 4 days at room temperature nor at 160° for 7 days. Vacuum fractionation of the volatile products recovered $(\text{CF}_3)_3\text{P}$ (0.424 g, 1.78 mmoles) (found M, 238; calcd for $(\text{CF}_3)_3\text{P}$, M, 238) which was collected at -116° and a mixture (0.091 g) of HCl and $(\text{CF}_3)_3\text{P}$ which was collected at -196° .

(f) With Methyl Mercaptan

A sample of $(\text{CF}_3)_3\text{P}$ (0.391 g, 1.64 mmoles) was allowed to react with CH_3SH (0.114 g, 2.37 mmoles) for 90 hours at 160°C . The volatile products were $(\text{CF}_3)_2\text{PSCH}_3$ which was collected at -84° and identified by n.m.r., $(\text{CF}_3)_3\text{P}$ and CH_3SH which was collected at -116° and CF_3H (0.033 g, 0.47 mmoles, 29%) which was collected at -196° .

(g) With Hydrogen Sulphide

$(\text{CF}_3)_3\text{P}$ (0.178 g, 0.75 mmoles) and H_2S (0.033 g, 0.97 mmoles) did not react during 11 days at 160° . However, after reacting the above mixture for 9 days at 185° , vacuum fractionation of the volatile products gave a mixture (0.004 g) of $(\text{CF}_3)_2\text{PSH}$ and $[(\text{CF}_3)_2\text{P}]_2\text{S}$ which was collected at -96° and identified by mass spectroscopy, a mixture (0.196 g) of $(\text{CF}_3)_3\text{P}$ and H_2S which was collected at both -116° and -132° and a mixture (0.001 g) of

$(\text{CF}_3)_3\text{P}$, H_2S and CF_3H which was collected at -196° .

(h) With Dimethylphosphine

$(\text{CF}_3)_3\text{P}$ (0.369 g, 1.55 mmoles) and $(\text{CH}_3)_2\text{PH}$ (0.097 g, 1.56 mmoles) did not react at room temperature for 4 days nor at 100° for 44 hours. Heating the samples at 185° for 4 days resulted in formation of a brown residue and a trace of CF_3H .

(i) With Dimethylarsine

$(\text{CF}_3)_3\text{P}$ (0.281 g, 1.18 mmoles) and $(\text{CH}_3)_2\text{AsH}$ (0.106 g, 1.00 mmoles) did not react at room temperature for 5 days. At 160° for 3 days a trace of CF_3H was found by i.r. spectroscopy. Further heating at 185° for 9 days resulted in almost quantitative recovery of a mixture (0.371 g) of $(\text{CF}_3)_3\text{P}$ and $(\text{CH}_3)_2\text{AsH}$. Some CF_3H (0.003 g, 0.04 mmoles) was collected at -196° .

(j) With Trimethylsilane

$(\text{CF}_3)_3\text{P}$ (0.434 g, 1.82 mmoles) and $\text{HSi}(\text{CH}_3)_3$ (0.152 g, 2.05 mmoles) did not react at room temperature for 11 days nor at 100° for 7 days. However, at 160° for 6 days the fractionation of the volatile products gave a mixture (0.054 g) of $(\text{CF}_3)_2\text{PSi}(\text{CH}_3)_3$ identified by n.m.r. and an unidentified compound which gave in the ^{19}F n.m.r. spectrum a doublet of doublets with $\phi = 47.3$ with $J' = 69$ cps and $J'' = 9.9$ cps, which was collected at -84° and

a mixture (0.435 g) of $(\text{CH}_3)_3\text{SiH}$ and $(\text{CF}_3)_3\text{P}$ which was collected at -116° , a mixture (0.088 g) of CF_3H and an unidentified compound which was collected at -196° . A dark brownish residue remained in the reaction tube.

(k) With Methanol

$(\text{CF}_3)_3\text{P}$ (0.457 g, 1.92 mmol) and MeOH (0.39 g, 1.22 mmol) did not react at room temperature for 3 months nor at 100° for 65 hours.

(l) With Ethanol

$(\text{CF}_3)_3\text{P}$ (0.434 g, 1.82 mmol) and $\text{C}_2\text{H}_5\text{OH}$ (0.103 g, 2.24 mmol) were reacted for 8 days at 160° . Vacuum fractionation of the volatile products gave a mixture (0.506 g) of $(\text{CF}_3)_3\text{P}$, $\text{C}_2\text{H}_5\text{OH}$, and a trace of CF_3H .

(m) With Phenol

A sample of $(\text{CF}_3)_3\text{P}$ (0.265 g, 1.11 mmol) was reacted with phenol (0.100 g, 1.06 mmol) for 3 days at room temperature. It resulted in almost quantitative recovery of $(\text{CF}_3)_3\text{P}$ (0.254 g, 1.07 mmol) which was collected at -116° .

Heating the reactants for 45 hours at 195° also resulted in almost quantitative recovery of $(\text{CF}_3)_3\text{P}$ (0.254 g, 1.07 mmol).

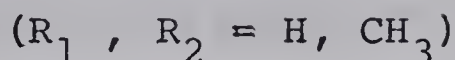
(n) With Pyridine-N-oxide

$(\text{CF}_3)_3\text{P}$ (0.480 g, 2.01 mmoles) and unpurified pyridine-N-oxide (0.35 g, 3.7 mmoles) did not react at room temperature for 12 hours. However at 70° for 6 hours, the volatile products were pyridine which was collected at -45° , an inseparable mixture (0.305 g) of $(\text{CF}_3)_3\text{P}$ and $(\text{CF}_3)_3\text{P}=\text{O}$ which was collected at -116° , and CF_3H (0.023 g, 0.33 mmoles) which was collected at -196° . A very volatile gas passed -196° trap and a brownish black oily residue remained in the reaction tube.

In another experiment purified pyridine-N-oxide (0.268 g, 2.82 mmoles) was allowed to react with $(\text{CF}_3)_3\text{P}$ (0.544 g, 2.32 mmoles) for 3 days at 70° . The volatile products were a mixture (0.218 g) of $(\text{CF}_3)_3\text{P}$, $(\text{CF}_3)_3\text{P}=\text{O}$, CF_3H and an unidentified product ($\phi = 78.8$ J = 80 cps) and some pyridine. A volatile gas passed the -196° trap and a black oily residue remained in the reaction tube.

2. Results and Discussion

Reactions of tris(trifluoromethyl)phosphine with several alcohols, acids and bases were explored. The most productive reactions of all were reactions of $(\text{CF}_3)_3\text{P}$ with ammonia and the methyl amines CH_3NH_2 and $(\text{CH}_3)_2\text{NH}$ at room temperature which gave several compounds in moderate yields according to eqn (1).



Harris⁴⁵ reported that $(\text{CF}_3)_3\text{P}$ reacted with NH_3 at -70° to give $(\text{CF}_3)_2\text{PNH}_2$ in moderate yield and a low volatile unidentified material. We have found that $(\text{CF}_3)_3\text{P}$ reacts with NH_3 at room temperature to form $(\text{CF}_3)_2\text{PNH}_2$ in agreement with Harris plus a small amount of a low volatile compound which was identified as the $[(\text{CF}_3)_2\text{P}]_2\text{NH}\cdot\text{NH}_3$ adduct by removal of the NH_3 and comparison of the properties of the purified product with those reported elsewhere.⁵¹ The bis(phosphino) amine has been prepared elsewhere from the reaction of $(\text{CF}_3)_2\text{PNH}_2$ with $(\text{CF}_3)_2\text{PCl}$ and $(\text{CH}_3)_3\text{N}$.⁵¹ The remaining amino compounds $(\text{CF}_3)_2\text{PN}(\text{H})\text{CH}_3$ and $(\text{CF}_3)_2\text{PN}(\text{CH}_3)_2$ were also obtained in moderate yields from the reactions of $(\text{CF}_3)_3\text{P}$ with H_2NCH_3 and $\text{HN}(\text{CH}_3)_2$ respectively thus providing an alternate route to the usual synthetic method involving the reactions⁴⁵ of $(\text{CF}_3)_2\text{PCl}$ with amines. The latter have the advantage of a greater reaction rate but do require the preparation of $(\text{CF}_3)_2\text{PCl}$.

The other reactions were not as productive as the amine reactions. Hydrogen bromide gave a trace of $(\text{CF}_3)_2\text{PBr}$ at 160° and a trace of $(\text{CF}_3)_2\text{PBr}$ and CF_3PBr_2 at 185° and with HCl no products were observed even at

160°. With the alcohols, no products were obtained when $(\text{CF}_3)_3\text{P}$ was allowed to react with phenol at 195° for 45 hours, with CH_3OH at 100° for 65 hours and $\text{C}_2\text{H}_5\text{OH}$ at 160° for 8 days. Similarly $(\text{CF}_3)_3\text{P}$ was recovered unchanged after treatment with $(\text{CH}_3)_2\text{PH}$ at 185° for 4 days and with $(\text{CH}_3)_2\text{AsH}$ at 185° for 9 days. However, even though $(\text{CF}_3)_3\text{P}$ did not react with $(\text{CH}_3)_3\text{SiH}$ at 100° for 7 days, reaction at 160° for 6 days gave some $(\text{CF}_3)_2\text{PSi}(\text{CH}_3)_3$ and an unidentified compound also in low yield. The compound $(\text{CF}_3)_2\text{PSi}(\text{CH}_3)_3$ has been previously reported and characterized by Grobe.⁴⁷ Methyl mercaptan reacted with $(\text{CF}_3)_3\text{P}$ after 90 hours at 160° to give $(\text{CF}_3)_2\text{PSCH}_3$ in 29% yield. The reaction of H_2S with $(\text{CF}_3)_3\text{P}$ did not proceed even after 11 days at 160° but after 9 days at 195° a trace of $(\text{CF}_3)_2\text{PSH}$ and $[(\text{CF}_3)_2\text{P}]_2\text{S}$ was found. Pyridine-N-oxide did not react with $(\text{CF}_3)_3\text{P}$ at room temperature but after heating to 70° for 6 hours, some $(\text{CF}_3)_3\text{P}=\text{O}$ was recovered in low yield with some CF_3H and a volatile gas that passed the -196° trap.

The ^{19}F and ^1H n.m.r. data (Table XIV, Appendix) were obtained for $(\text{CF}_3)_2\text{PN}(\text{H})\text{CH}_3$ ⁴⁸, $(\text{CF}_3)_2\text{PN}(\text{CH}_3)_2$ ⁴⁸, $[(\text{CF}_3)_2\text{P}]_2\text{NH}$, $[(\text{CF}_3)_2\text{P}]_2\text{NH}\cdot\text{NH}_3$ adduct and $(\text{CF}_3)_2\text{PNH}_2$. Of much interest is the low temperature ^1H n.m.r. spectra of $(\text{CF}_3)_2\text{PNH}_2$ shown in Figure 6. At room temperature, the compound $(\text{CF}_3)_2\text{PNH}_2$ gave a broad singlet at $\tau = 7.4$.

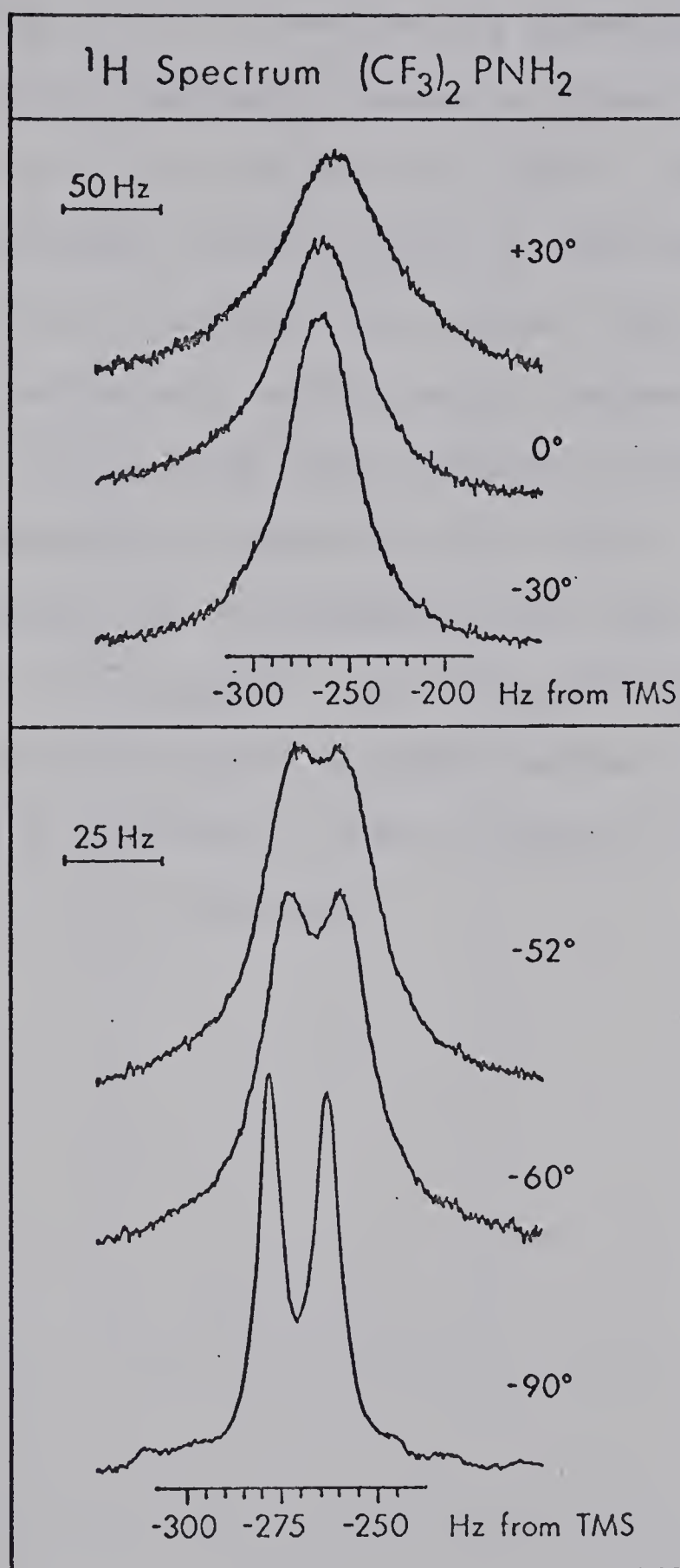


FIGURE 6. Low temperature ^1H n.m.r. spectra of $(\text{CF}_3)_2\text{PNH}_2$.

Further cooling to -47° resulted in appearance of a doublet separation which eventually became a clearly resolved doublet ($\tau = 7.32$, $J = 15$ cps) at -110° . Rapid exchange between the protons on $(\text{CF}_3)_2\text{PNH}_2$ at room temperature gives rise to the characteristic broad line. Upon cooling the rate of exchange is sufficiently reduced to resolve the P-H coupling ($^2J_{\text{PH}}$) with good resolution being achieved at the lowest accessible temperature of -110° . The P-H coupling obtained is in agreement with that observed in $(\text{CF}_3)_2\text{PSH}$ ⁴⁰, $(\text{CF}_3)_2\text{PS}_2\text{H}$ ²⁹ and $(\text{CF}_3)_2\text{PN}(\text{H})\text{CH}_3$.^{48,49} N.m.r. spectrum of the N-bridged phosphino amine is shown in Figure 7 and is similar to that of other $[(\text{CF}_3)_2\text{P}]_2\text{X}$ ⁵² molecules ($\text{X} = \text{O}, \text{S}, \text{nothing}$).

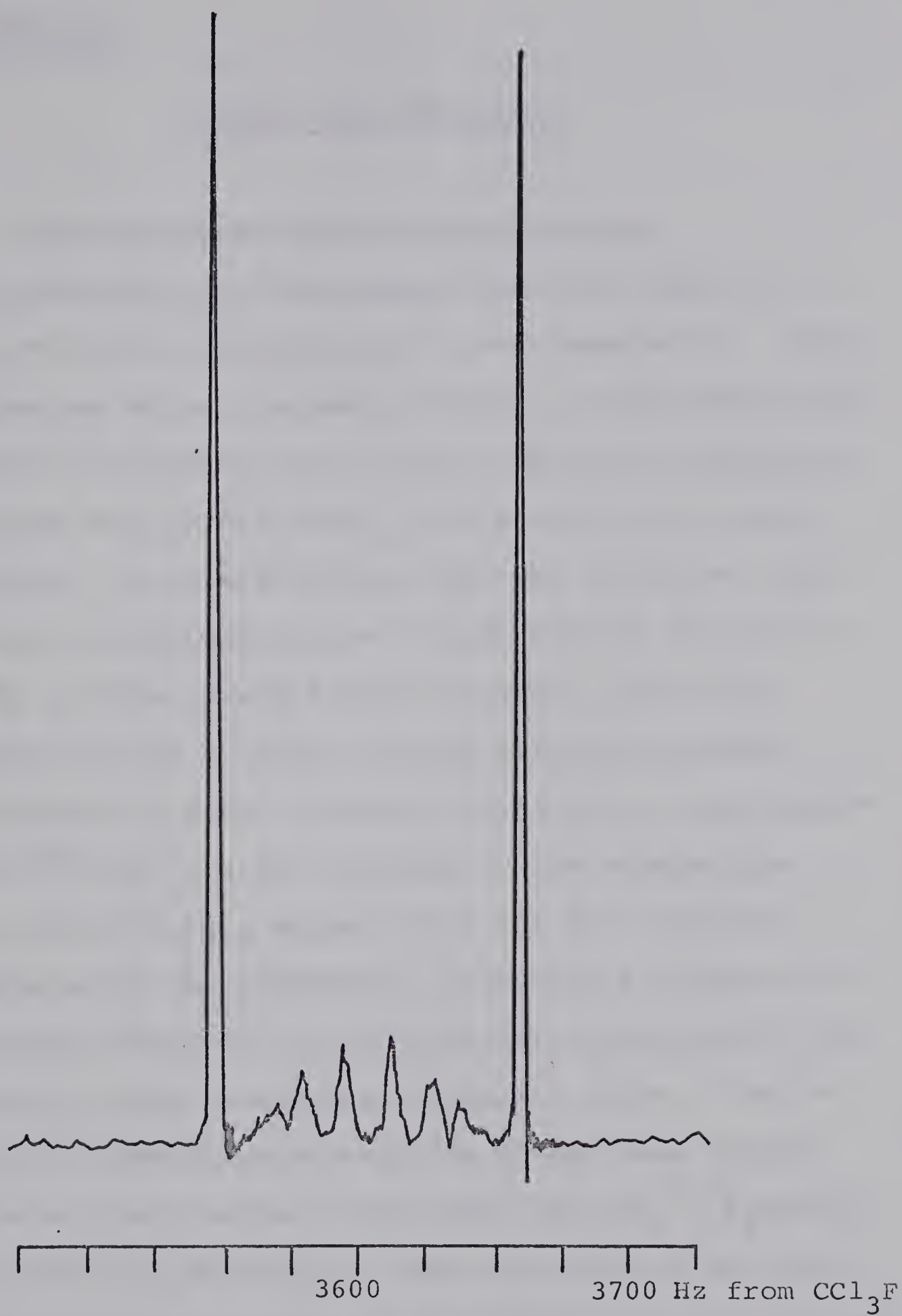


FIGURE 7 N.m.r. spectrum of $[(\text{CF}_3)_2\text{P}]_2\text{NH}$
at 56.4 MHz.

CHAPTER VIISUMMARY AND CONCLUSION

The new pentacoordinated phosphorane, $(\text{CF}_3)_3\text{P}[\text{OSi}(\text{CH}_3)_3]_2$ was prepared from the reaction of $(\text{CF}_3)_3\text{P}=\text{O}$ with $[(\text{CH}_3)_3\text{Si}]_2\text{O}$ at room temperature. This phosphorane while reasonably stable at room temperature thermally decomposes to the new pentavalent phosphoryl compound $(\text{CF}_3)_2\text{P}(\text{O})\text{OSi}(\text{CH}_3)_3$ and a variety of other products. It is significant that the strong $\text{P}=\text{O}$ bond has been sacrificed for two $\text{P}-\text{O}-\text{Si}$ bridges in the synthesis of this compound which suggests that $\text{P}-\text{O}-\text{Si}$ bridges provide a strong bonding situation perhaps accentuated by some π bonding interaction. Low temperature ^{19}F and ^1H n.m.r. studies of the phosphorane $(\text{CF}_3)_3\text{P}[\text{OSi}(\text{CH}_3)_3]_2$ suggest that the most probable structure for the phosphorane (assuming a trigonal bipyramidal framework) is the structure with both of the $\text{OSi}(\text{CH}_3)_3$ groups occupying equatorial sites. The reaction of dimethylamine with the phosphorane cleaves the strong $\text{O}-\text{Si}$ bonds to give the $(\text{CF}_3)_2\text{PO}_2^- \text{ } ^+\text{H}_2\text{N}(\text{CH}_3)_2$ salt and $(\text{CH}_3)_3\text{SiN}(\text{CH}_3)_2$. This reaction was the most straightforward reaction of the phosphorane and provided further evidence for its formula. Many other reactions remain to be done with this phosphorane which should

provide more chemical knowledge of this interesting system.

The new compound $(\text{CF}_3)_2\text{P}(\text{O})\text{OSi}(\text{CH}_3)_3$, first obtained by thermal decomposition of $(\text{CF}_3)_3\text{P}[\text{OSi}(\text{CH}_3)_3]_2$, was prepared almost quantitatively from the reaction of $(\text{CF}_3)_2\text{P}(\text{O})\text{Cl}$ with $[(\text{CH}_3)_3\text{Si}]_2\text{O}$ at 100° . In contrast, the less stable sulphur analogue $(\text{CF}_3)_2\text{P}(\text{S})\text{SSi}(\text{CH}_3)_3$ could be obtained only in moderate yield from the reaction of $(\text{CF}_3)_2\text{PS}_2\text{H}$ with $[(\text{CH}_3)_3\text{Si}]_2\text{NH}$ at room temperature but the analogous reaction of the chlorofluorophosphoryl compound did not provide good yields. The resultant $(\text{CF}_3)_2\text{P}(\text{E})\text{ESi}(\text{CH}_3)_3$ ($\text{E} = \text{O}, \text{S}$) reacted with HCl and $(\text{CH}_3)_2\text{NH}$. Dimethylamine cleaved the O-Si and S-Si bonds readily giving the anion salts and $(\text{CH}_3)_3\text{SiN}(\text{CH}_3)_2$. With HCl , $(\text{CF}_3)_2\text{P}(\text{S})\text{SSi}(\text{CH}_3)_3$ was cleaved quantitatively at the S-Si bond to give $(\text{CH}_3)_3\text{SiCl}$ and the thio-acid. Although $(\text{CF}_3)_2\text{P}(\text{O})\text{OSi}(\text{CH}_3)_3$ was cleaved at the O-Si bond to give the analogous products, the majority of $(\text{CF}_3)_2\text{P}(\text{O})\text{OSi}(\text{CH}_3)_3$ was recovered unreacted.

Several attempts were made to prepare the mixed oxythio compounds having $\text{P}(\text{O})\text{SSi}$ or $\text{P}(\text{S})\text{OSi}$ units but without much success. All of the avenues of exploration have not been exhausted yet. For example it appears possible that compounds containing $\text{P}(\text{O})\text{SSi}$ or $\text{P}(\text{S})\text{OSi}$ structures might result from the reaction of

$(\text{CF}_3)_2\text{P}(\text{S})\text{OH}$ with $[(\text{CH}_3)_3\text{Si}]_2\text{NH}$.

The reaction of $(\text{CF}_3)_2\text{PCl}$ with $[(\text{CH}_3)_3\text{Si}]_2\text{S}$ at 100° gave the new compound $(\text{CF}_3)_2\text{PSSi}(\text{CH}_3)_3$ which is the first example of a trivalent phosphorus compound containing the P-S-Si bridge. The more stable oxygen analogue

$(\text{CF}_3)_2\text{POSi}(\text{CH}_3)_3$ was best prepared from the reaction of $(\text{CF}_3)_2\text{PF}$ with $[(\text{CH}_3)_3\text{Si}]_2\text{O}$ at 100° . Significantly, the reactions of $(\text{CF}_3)_2\text{POSi}(\text{CH}_3)_3$ and $(\text{CF}_3)_2\text{PSSi}(\text{CH}_3)_3$ with $(\text{CH}_3)_2\text{NH}$ and HCl showed marked differences. The compound $(\text{CF}_3)_2\text{PSSi}(\text{CH}_3)_3$ is more reactive and is cleaved almost quantitatively at the S-Si bond by both $(\text{CH}_3)_2\text{NH}$ and HCl . The products obtained in the former case are $(\text{CF}_3)_2\text{PSH}$ (obtained as the dimethylamine adduct) and $(\text{CH}_3)_3\text{SiN}(\text{CH}_3)_2$. The latter reaction gave $(\text{CF}_3)_2\text{PSH}$ and $(\text{CH}_3)_3\text{SiCl}$. In contrast, HCl attacked both the O-Si and P-O bonds in $(\text{CF}_3)_2\text{POSi}(\text{CH}_3)_3$ to give $(\text{CF}_3)_2\text{POH}$, $(\text{CF}_3)_2\text{PCl}$, $(\text{CH}_3)_3\text{SiCl}$ and $[(\text{CH}_3)_3\text{Si}]_2\text{O}$ but the majority of $(\text{CF}_3)_2\text{POSi}(\text{CH}_3)_3$ was recovered unreacted. With $(\text{CH}_3)_2\text{NH}$, only 12% of $(\text{CF}_3)_2\text{POSi}(\text{CH}_3)_3$ was cleaved at the O-Si bond to give $(\text{CH}_3)_3\text{SiN}(\text{CH}_3)_2$ and the dimethylamine adduct of $(\text{CF}_3)_2\text{POH}$; the remaining 88% of the $(\text{CF}_3)_2\text{POSi}(\text{CH}_3)_3$ reacted at the P-C bond with $(\text{CH}_3)_2\text{NH}$ to give CF_3H and the new compound $\text{CF}_3\text{P}[\text{OSi}(\text{CH}_3)_3]\text{N}(\text{CH}_3)_2$ which contains both the $\text{N}(\text{CH}_3)_2$ and $\text{OSi}(\text{CH}_3)_3$ substituents on tervalent phosphorus.

Reactions of $(\text{CF}_3)_3\text{P}$ with several protonic reagents (acids, alcohols and bases) were attempted. Only the amines reacted appreciably with $(\text{CF}_3)_3\text{P}$ to give moderate yields of the amino-phosphorus compounds suggesting that the tristrifluoromethylphosphine is susceptible to attack only by strongly basic protonic reagents.

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A P P E N D I X

TABLE XIV

Summary of the N.M.R. Parameters of the Compounds Prepared in this Study

Compound	^{19}F a		^1H b		^{31}P c	
	ϕ	J_{PF}	τ	J	Δ	J
$(\text{CF}_3)_3\text{P}[\text{OSi}(\text{CH}_3)_3]_2$	69.9	108.8 ^d	9.55	-	205.8	108.7 ^e
$(\text{CF}_3)_2\text{P}(\text{O})\text{OSi}(\text{CH}_3)_3$	73.1	121.3 ^d	9.47	-	143.4	121.4 ^f
$(\text{CF}_3)_2\text{P}(\text{S})\text{SSi}(\text{CH}_3)_3$	71.6	105.0 ^d	9.24	-	66.4	105.0 ^g
$(\text{CF}_3)_2\text{POSi}(\text{CH}_3)_3$	67.4	85.0 ^d	9.62		30.3	85.0 ^h
$(\text{CF}_3)_2\text{PSSi}(\text{CH}_3)_3$	58.7	79.5 ^d	9.39	1.3 ^d	91.2	79.0 ⁱ
$\text{CF}_3\text{P}[\text{OSi}(\text{CH}_3)_3]_3\text{N}(\text{CH}_3)_2$	72.2	81.5 ^k	$\begin{cases} 7.19 & 8.9^l \\ 9.67 & 0.3^m \end{cases}$		8.7	$\sim 80^j$
$(\text{CF}_3)_2\text{PNH}_2$	66.3	82.0 ^d	$\begin{cases} 7.40 & - \\ 7.32^n & 15^n \end{cases}$			
$[(\text{CF}_3)_2\text{P}]_2\text{NH}\cdot\text{NH}_3$	62.9	89.3 ^p	7.04	-		
$[(\text{CF}_3)_2\text{P}]_2\text{NH}$	64.3	90.0 ^p	5.60 ^q			
$(\text{CF}_3)_2\text{PN}(\text{H})\text{CH}_3$	64.5	82.4 ^d				
$(\text{CF}_3)_2\text{PN}(\text{CH}_3)_2$	59.8	86.5 ^d	7.03	9.0 ^d		

(continued.....)

- (a) ϕ vs CFCl_3
- (b) τ vs TMS
- (c) Δ vs P_4O_6
- (d) Doublet spin splitting pattern
- (e) Intensity ratios observed 8.9:33.0:80.8:120.0:126.0:85.4:33.5:9 ;
calcd for decet splitting pattern 1:9:36:84:126:126:84:36:9:1.
- (f) Intensity ratios observed 0.9:6.8:15.1:21.0:15.7:5.8:1.0 ;
calcd for septet splitting pattern 1:6:15:20:15:6:1.
- (g) Intensity ratios observed 5.3:14.6:23.4:15.0:4.4. The noise level was high. Calcd for septet splitting pattern 1:6:15:20:15:6:1.
- (h) Intensity ratios observed 0.9:6.0:14.6:20.0:14.6:6.7:1.2; Calcd for septet splitting 1:6:15:20:15:6:1.
- (i) Intensity ratios observed 1.1:6.2:15.7:20.1:15.3:6.8:1.2; Calcd for septet splitting pattern 1:6:15:20:15:6:1
- (j) Observed as weak quartet ($J \sim 80$) with undiscernable finer detail (high noise level).
- (k) Doublet ($J = 81.5$) of septets ($J = 8.9$).
- (l) Doublet ($J = 8.9$) of quartets ($J = 0.9$) for dimethylamine proton.
- (m) Simple doublet ($J = 0.3$) for trimethylsilyl protons.
- (n) Values obtained at -110°
- (p) Symmetric complex as shown in Figure 6.
- (q) Value obtained at 0° .

TABLE XVObserved and Calculated Vapor Pressures for Water

Temp °C	Pressure (mm)	
	Obs	Calcd ^a
22.0	20.90	20.47
23.4	21.86	22.24
46.3	78.58	77.53
51.1	98.09	98.50
51.7	101.60	101.45
61.3	150.53	160.14
63.7	179.29	178.77
66.2	200.56	200.15
70.5	241.59	242.16
75.3	299.67	297.88
78.7	345.18	343.77
80.0	365.63	362.86
81.3	385.27	382.86
84.7	440.76	439.73
86.6	479.07	474.57
89.7	535.91	536.52

^a Calculated from derived least squares equation given on page 5.

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